

# New Anionic Rearrangements. XVII. 1,2-Anionic Rearrangements from Oxygen to Carbon in Benzyloxyorganosilanes and Benzyloxyorganogermanes<sup>1,2</sup>

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**Abstract:** Benzyloxytrimethylsilane (**1a**), benzyloxytrimethylgermane (**1h**), trimethylgermyloxydiphenylmethane (**1j**), and various related compounds, upon metalation at the benzyl carbon atom with excess *tert*-butyllithium or lithium diisopropylamide in tetrahydrofuran, rearrange rapidly *via* a 1,2-shift of silicon or germanium to the  $\alpha$  carbanion to give, in high yield, anions of  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**2a**),  $\alpha$ -hydroxy- $\alpha$ -trimethylgermyltoluene (**2h**), and trimethylgermyldiphenylmethanol (**2j**), respectively. These anions can be protonated, alkylated, or silylated at oxygen except for **1a**, which alkylates abnormally at carbon despite protonation and silylation at oxygen. Trimethylsilyloxydiphenylmethane (**1g**) is readily metalated, but subsequent rearrangement does not occur. **2a**, but not **2h**, undergoes a Brook rearrangement in the presence of a catalytic amount of sodium-potassium alloy, forming **1a** in high yield. In this catalytic rearrangement, the neutral species **2a** and **1a** are being equilibrated, and the high strength of the Si-O bond in **1a** makes this the thermodynamically favored isomer. In the anion rearrangement, the anions of **2a** and **1a** are being equilibrated, and the preference of the negative charge to be located on oxygen, rather than on carbon, makes the anion of **2a** the favored isomer at equilibrium. 2-Trimethylsilyloxypropionitrile, upon metalation, appears not to undergo significant rearrangement.

The migratory aptitude of silicon in 1,2-anionic rearrangements<sup>4</sup> of silylhydrazines<sup>5</sup> and silylhydroxylamines<sup>6</sup> is remarkable. When alkyl carbon migrates to an anionic site, a simple [1,2]-sigmatropic suprafacial shift is disallowed by the Woodward-Hoffmann rules,<sup>7,8</sup> and migration is slow. However, when silicon migrates, rearrangement may occur without the above symmetry restrictions through a pentacoordinate transition state<sup>9</sup> and migration can be fast.

Many known 1,2-anionic carbon rearrangements should have organosilicon counterparts.<sup>10</sup> One such carbon rearrangement is the well-known Wittig rearrangement of an ether to its isomeric alcohol which can occur upon metalation with excess organolithium reagent.<sup>11,12</sup> Here migration of carbon from oxygen to an  $\alpha$  carbanion occurs. Alkyl migrations take place rather slowly, and yields are reduced significantly by side reactions.<sup>13</sup> The mechanism is now thought to involve

an intramolecular radical pair cleavage-recombination process.<sup>8</sup>

In this paper we report anionic rearrangements of the Wittig type where silicon is the migrating atom. Thus, benzyloxytrialkylsilanes and benzyloxytrialkylgermanes **1**, lithiated at their benzyl carbons, undergo rapid isomerizations to oxyanions of  $\alpha$ -hydroxy- $\alpha$ -trialkylsilyltoluenes and  $\alpha$ -hydroxy- $\alpha$ -trialkylgermyltoluenes **2** in high yield (**1'**  $\rightarrow$  **2'**, Scheme I). The results are discussed in relation to the well-known anti-Wittig (Brook) rearrangement of  $\alpha$ -silylcarbinols to alkoxysilanes that can occur in high yield when *neutral* species are equilibrated in the presence of *catalytic* amounts of base<sup>9</sup> (**2**  $\rightarrow$  **1**, M = Si).

## Metalations

Metalation of the compounds listed in Table I occurs as outlined in Scheme I. Throughout this paper, products are identified systematically by a number (for structure type), a prime (if an anion), a letter (to identify substituents, as listed in Table I), and the identity of derivative groups if other than H. Thus, for example, the methyl derivative of anion **1a'** is **1a** ( $R'' = \text{CH}_3$ ).

In order to study the actual rearrangements of carbanion **1'** to **2'** it was necessary first to develop techniques for metalating compounds **1** rapidly and selectively at the benzylic position (**1**  $\rightarrow$  **1'**). The desired metalation can be complicated by the reaction of the alkyllithium reagent with the alkoxysilane either to cleave the silicon-oxygen bond<sup>14</sup> (**1**  $\rightarrow$  **3'**) or to metalate the slightly acidic methyl groups attached to silicon (**1**  $\rightarrow$  **4'**).<sup>15</sup> **1** can therefore appear in the anion solution as unreacted **1**, the unrearranged benzyl anion **1'**, the rearranged benzyl anion **2'**, the cleavage product **3'**, and the silylmethyl metalated compound **4'**. The presence

(1) This work was supported in part by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 70-1904.

(2) Previous paper in this series: A. Wright, D. Ling, P. Boudjouk, and R. West, *J. Amer. Chem. Soc.*, **94**, 4784 (1972).

(3) Procter and Gamble Fellow, 1972-1973.

(4) For a review of silyl anionic rearrangements, see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

(5) R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, **89**, 4072 (1967).

(6) R. West, P. Boudjouk, and A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969).

(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(8) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(9) A. G. Brook, G. E. Legrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

(10) The reverse possibility that known organosilicon anionic rearrangements could have carbon counterparts, despite differences in mechanism, has been realized in the recently discovered aryl hydrazine anion rearrangement,<sup>10</sup> whose discovery was stimulated by the observation of the silyl hydrazine rearrangement.<sup>5</sup> See R. West and H. F. Stewart, *J. Amer. Chem. Soc.*, **92**, 853 (1970).

(11) G. Wittig and L. Löhmann, *Justus Liebigs Ann. Chem.*, **550**, 260 (1942).

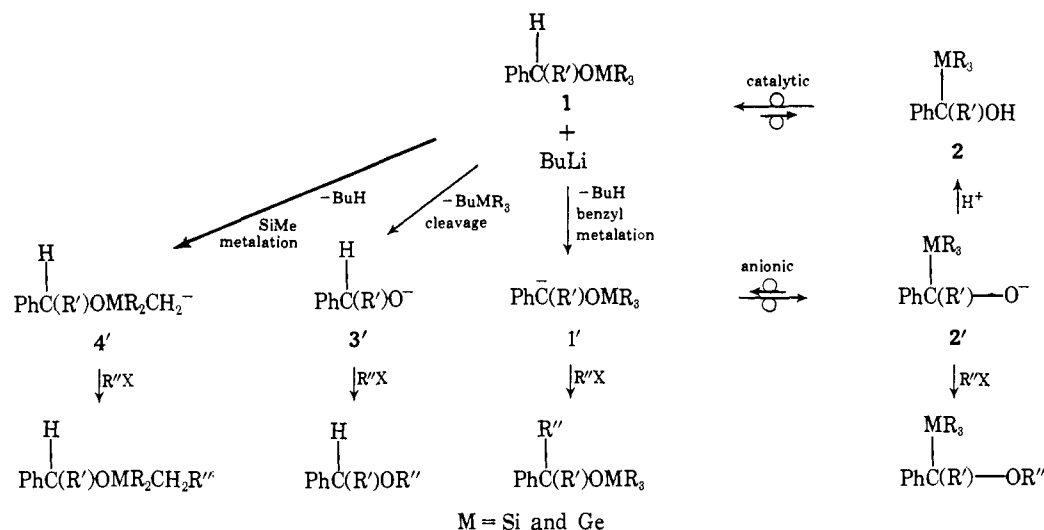
(12) D. L. Dalrymple, T. L. Kruger, and W. N. White in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967, p 617.

(13) H. Schäfer, U. Schöllkopf, and D. Walters, *Tetrahedron Lett.*, 2809 (1968).

(14) This cleavage reaction has actually been used as a synthetic method for forming silicon-carbon bonds; see C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 12 and 13.

(15) J. W. Connally and G. Urry, *Inorg. Chem.*, **2**, 645 (1963); D. J. Peterson, *J. Organometal. Chem.*, **1**, 373 (1967); G. E. Hartwell and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4625 (1966).

Scheme I



of these anions can be inferred from the compositions of the solutions resulting from quenching the anions with protonating, alkylating, or silylating agents. Table I shows the amounts of each derivative isolated, listed under the species in the anion solution from which it is derived. Percentages are based on the total of all species originating from **1** appearing in solution. Anion solutions derivatized with acid provide less information than those quenched with alkylating or silylating reagents, because acid quenching results in the isolation of **1** from **1'** and **4'** as well as from unreacted **1**.

From each particular anion solution the same distribution of derivatives of **3'** and **4'** was obtained for all silylating and alkylating reagents used. Therefore, **3'** and **4'** are not in rapid equilibrium with each other or with any other anion in solution, for if they were the final product distributions would be determined in part by the relative rates of derivatization of equilibrating anions. Because these relative rates would almost certainly vary with choice of alkylating or silylating agent, constant product distributions would probably not have been obtained. The equilibration of **1'** with **2'** will be discussed later.

The products of metalation vary with the identity of the compound being metalated and the conditions of metalation. Benzyloxytriethylsilane (**1b**) is metalated by *tert*-butyllithium in pentane very slowly at 25° but selectively at the benzyl position.<sup>16</sup> Under these conditions, however, benzyloxytrimethylsilane (**1a**) is metalated slowly at a silicon methyl group giving predominately **4a'**,<sup>17</sup> as evidenced by the observation of the SiCH<sub>2</sub>Li proton resonance at  $\tau$  12.07<sup>15</sup> in the solution and by isolation of a trialkylchlorosilane derivative. If tetramethylethylenediamine (TMEDA)<sup>18</sup> is present in the reaction medium, **1a** is metalated quickly at 25° giving 44% benzyl metalation (**1a'** + **2a'**), 23% **3a'**, and only 34% **4a'**. At -23°, 60% **1a'** + **2a'**, 16% **3a'**, and 21% **4a'** are formed (Table I). Generally, low temperature disfavors **4'** formation but also reduces the

rate of over-all reaction. When *n*-butyllithium was used with TMEDA as metalation reagent, it was found that alkoxyasilanes were predominantly cleaved to **3'**, unless the substituents on silicon were bulky.<sup>19</sup> Thus 100% cleavage occurs in **1a**, 22% in **1b**, and none in benzyloxy-*tert*-butyldimethylsilane (**1c**).

The optimum conditions for metalation of most compounds involve the use of *tert*-butyllithium in tetrahydrofuran (THF) solution at low temperatures. Thus, in 1:1 THF-pentane solution, **1a** is metalated by *tert*-butyllithium at -50° in less than 2 min giving 95% **1a'** + **2a'**. Metalation in polar THF solution is convenient since subsequent alkylations and silylations proceed much more rapidly and cleanly than in pentane. On the other hand, *tert*-butyllithium reacts slowly with THF so that at the higher temperatures and longer times required to metalate hindered species such as **1c**, **1d**, **1f**, and **1g**, *tert*-butyllithium is entirely consumed before all of the starting compound is metalated. The half-time for the decomposition of *tert*-butyllithium in 1:1 pentane-THF is about 6 hr at -23°.

The rate of benzyl metalation is very sensitive to steric factors. Thus, even **1b** is metalated more slowly than **1a**. 1-Phenyl-1-trimethylsiloxyethane (**1e**) can be metalated to form **1e'** + **2e'** in 29% yield, but replacing the  $\alpha$ -methyl group in **1e** with the slightly acidifying but bulkier trimethylsilyl group as in **1f** prevents any benzyl metalation from occurring, regardless of reaction conditions used. Trimethylsiloxydiphenylmethane (**1g**) can be metalated in good yield only between -20 and -30°; the high acidity of the diphenylmethyl proton is offset by the steric hindrance around the tertiary carbon atom.

Metalation of alkoxygermanes **1h** and **1j** proceeds easily in *tert*-butyllithium-THF solution with predominant benzyl metalation. Significant cleavage to **3'** also occurs, undoubtedly because of the weak germanium-oxygen bond. As is characteristic of germanium compounds, germyl-methyl metalation does not occur, probably because of reduced d <sub>$\pi$</sub> -p <sub>$\pi$</sub>  backbonding in the anion.<sup>20</sup>

*tert*-Butyllithium in THF rapidly cleaves dimethyl-

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

(17) H. F. Stewart, Ph.D. Thesis, University of Wisconsin, Madison, 1969.

(18) TMEDA increases the basicity of organolithium compounds by coordinating to lithium, increasing the polarity of the Li-C bond; see G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, 3rd ed, Methuen and Co., Ltd., London, 1960, p 18.

(19) R. West and G. A. Gornowicz, *J. Organometal. Chem.*, **28**, 25 (1971).

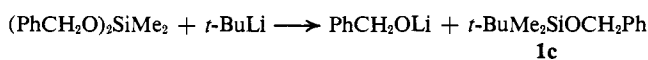
(20) F. Glockling, "The Chemistry of Germanium," Academic Press, London, England, 1969, Chapter 1.

Table I. Anionic Rearrangements

Compd	MR <sub>3</sub>	R'	R''-X <sup>c</sup>	Metalation conditions																					
				Yields of anion derivatives, <sup>a</sup> %																					
				<i>tert</i> -BuLi, pentane, THF				<i>tert</i> -BuLi, pentane, TMEDA					LiN( <i>i</i> -propyl) <sub>2</sub> , hexane, THF				<i>n</i> -BuLi, hexane, TMEDA								
1	1'	2'	3'	4' <sup>b</sup>	1	1'	2'	3'	4'	1	1'	2'	3'	4'	1	1'	2'	3'	4'						
<b>1a</b>	SiMe <sub>3</sub>	H	H-OAc	0	0	95	1	4	3	0	61	13	23	2	0	84	14	0	0	0	0	100	0		
			Et <sub>3</sub> Si-Cl	0	0	96	2	2	3	0	60	16	21												
			CH <sub>3</sub> -I	0	91	7	1	1																	
			CH <sub>3</sub> -SO <sub>4</sub> Me	0	36	62	1	1																	
<b>1b</b>	SiEt <sub>3</sub>	H	H-OAc	2	0	97	1	0							13	0	65	22	0						
			Me <sub>3</sub> Si-Cl	0	0	100	0	0																	
			CH <sub>3</sub> -I	0	99	1	0	0																	
			CH <sub>3</sub> -SO <sub>4</sub> Me	0	40	60	0	0																	
<b>1c</b>	SiMe <sub>2</sub> - <i>t</i> -Bu	H	H-OAc	30	0	70	0	0	0	0	64	0	36	46	0	54	0	0	5	0	85	0	10		
<b>1d</b>	SiPh <sub>3</sub>	H	H-OAc	6	0	61	7	0																	
<b>1e</b>	SiMe <sub>3</sub>	CH <sub>3</sub>	H-OAc	5	0	29	56	0						94	0	2	4	0							
<b>1f</b>	SiMe <sub>3</sub>	SiMe <sub>3</sub>	H-OAc	60	0	0	10	30	38	0	0	4	58												
<b>1g</b>	SiMe <sub>3</sub>	Ph	H-OAc	13	77	0	10	0																	
			CH <sub>3</sub> -I	13	75	0	12	0																	
			H-OAc	0	0	71	29	0								0	0	70	30	0					
			CH <sub>3</sub> -I	0	0	83	17	0																	
<b>1h</b>	GeMe <sub>3</sub>	H	H-OAc	0	0	71	29	0																	
			CH <sub>3</sub> -I	0	0	83	17	0																	
			CH <sub>3</sub> -SO <sub>4</sub> Me	0	0	73	27	0																	
			H-OAc	0	0	70	30	0																	
<b>1j</b>	GeMe <sub>3</sub>	Ph	H-OAc	0	0	70	30	0																	
			CH <sub>3</sub> -I	0	0	73	27	0																	

<sup>a</sup> Derivatives are listed under the species in the anion solution from which they are believed to be derived. <sup>b</sup> Except for **1a**, where an actual derivative of 4' was isolated and characterized, the amounts of 4' present in the anion solution were estimated from the pmr spectrum of the anion solution. <sup>c</sup> Protonation of anion solutions not containing THF was accomplished by addition of aqueous 2 M MgCl<sub>2</sub> solution at -22°.

dibenzoyloxysilane forming **1c** and from metalation of **1c** some **2c'**.



Lithium diisopropylamide in THF solution, a reagent both easier to handle and less expensive than *tert*-butyllithium, metalates several representative silanes and germanes slowly at the benzyl position (Table I). Temperatures of between 0 and 25° are required to effect metalation (Table II), some cleavage occurring under

Table II. Anionic Rearrangements (Time (hr) and Temperature (°C) of Metalations)

Compd	Metalation conditions			
	<i>tert</i> -BuLi, pentane, THF	<i>tert</i> -BuLi, pentane, TMEDA	LiN( <i>i</i> -propyl) <sub>2</sub> , hexane, THF	<i>n</i> -BuLi, hexane, TMEDA
<b>1a</b>	0.03 (-50)	3.00 (-23)	12.00 (25)	0.17 (-23)
<b>1b</b>	0.50 (-40)			0.13 (25)
<b>1c</b>	1.33 (-23)	7.00 (25)	18.00 (25)	2.00 (25)
<b>1d</b>	18.00 (-40)			
<b>1e</b>	13.00 (-30)		12.00 (25)	
<b>1f</b>	0.50 (-23)	0.67 (25)		
<b>1g</b>	2.00 (-20)			
<b>1h</b>	0.17 (-78)			
<b>1j</b>	2.00 (-20)		48.00 (25)	

these conditions to form **3'**. Fortunately, THF is stable to the base at 25°. Also no metalation of the SiCH<sub>3</sub> moiety occurs to produce **4'**. The metalation is probably reversible and goes to completion only because **1'** is continuously removed from solution by rearrangement to **2'**. Supporting the hypothesis of an equilibrium is the fact that the pK<sub>a</sub> of ammonia is about 36<sup>21</sup> and that of benzyloxytrimethylsilane (**1a**), for example, is probably almost the same, since toluene has a pK<sub>a</sub>

(21) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 1.

of 35,<sup>21</sup> and there should be no further acidification at the benzyl position of **1a** due to the presence of the α-oxygen atom.<sup>22</sup>

### Rearrangements

(a) **Silicon-Oxygen Rearrangements.** The discussion will refer to systems metalated in THF-pentane solution by *tert*-butyllithium at low temperature unless otherwise indicated (Table II). Acid quenching of a solution of **1a** 2 min after metalation yields **2a** in 95% yield. The absence of **1a** as a product indicates that the metalation of **1a** to form **1a'** is complete within 2 min and that there follows a fast isomerization of **1a'** to **2a'** either before or during derivatization. This represents the first example of a 1,2-anionic rearrangement from oxygen to an α carbanion in which silicon is the migrating group. The rearrangement is much faster than the Wittig rearrangement of benzyl methyl ether and occurs more selectively. Both **1a** and **2a** give, when metalated, almost colorless solutions having identical nmr spectra. The resonances are somewhat broadened (~6 Hz), possibly due to self-association of the anion into oligomers. Only one trimethylsilyl resonance is observed at τ 10.18, even at -82°. There is therefore either only one major anion species present or those present are in rapid equilibrium. A resonance at τ 5.30, integrating to one proton, is due to the one benzyl proton remaining after metalation; the phenyl proton resonances occur at τ 2.88. If the anion were of the form **1a'**, the phenyl proton resonances should be influenced by the α carbanion. For example, there is a considerable upfield shift in the phenyl proton resonances of benzyllithium in THF from those in toluene due to the introduction of electron density into the ring from the carbanion (Table III).<sup>23</sup> SCF molecular orbital calculations predict the correct upfield shifts.

(22) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969).

(23) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

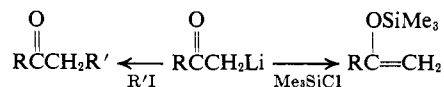
**Table III.** Phenyl Proton Nmr Resonances,  $\tau$ 

Hydro-carbon		Silane		Germane	
PhCH <sub>3</sub>	3.32	<b>1a</b>	2.86	<b>1h</b>	2.70
PhCH <sub>2</sub> Li	3.80, 4.50	<b>2a'</b>	2.88	<b>2h'</b>	2.81
		<b>2a</b>	2.87	<b>2h</b>	2.90
Ph <sub>2</sub> CH <sub>2</sub>	2.85	<b>1g</b>	2.84	<b>1j</b>	2.82
Ph <sub>2</sub> CHLi	3.47, 4.35	<b>1g'</b>	2.42-3.49, 4.39	<b>2j'</b>	2.42-3.16
				<b>2j</b>	2.30-3.02

Since there is practically no upfield shift in the phenyl proton resonances of the anion of **1a** and **2a** the anion must be mainly in the form **2a'**.<sup>24</sup>

Although the anion **2a'**, prepared from **1a**, upon treatment with triethylchlorosilane at  $-22^\circ$  slowly gives **2a** ( $R'' = Et_3Si$ ) as expected, with methyl iodide **2a'** slowly gives *unrearranged* **1a** ( $R'' = CH_3$ ) at  $25^\circ$ . Methyl sulfate gives a mixture of **1a** ( $R'' = CH_3$ ) and **2a** ( $R'' = CH_3$ ). Significantly, quenching with methyl iodide and methyl sulfate gives product distributions invariant whether the anion is prepared by metalation of **1a** or **2a**. These results prove that there is at least a small amount of **1a'** present in solution and that **1a'** and **2a'** are in equilibrium with each other. The fact that  $CH_3I$  reacts with the anion solution only slowly suggests that the amount of **1a'** present is small, since it is known that carbanions normally react rapidly with methyl iodide in polar solvents.<sup>25</sup>

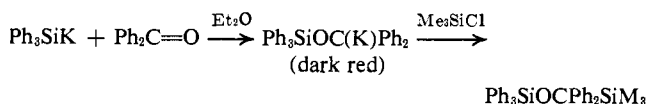
The preference for C alkylation but O silylation of **2a'** has precedent in enolate chemistry. Lithium enolates of ketones are nearly always alkylated at carbon by alkyl halides,<sup>25</sup> but derivatization with trialkylchlorosilane produces the silylated enol.<sup>26</sup>



Benzyloxytriethylsilane (**1b**) rearranges in exactly the same fashion as **1a**. Alkoxysilanes **1c**, **1d**, and **1e** also undergo rearrangement. Alkoxysilane **1f** cannot be metalated at the benzyl position. The rearrangement thus appears to be general for benzyloxysilanes provided metalation can occur at a benzyl proton.

To test the intramolecularity of the rearrangement, **1a** and *p*-isopropylbenzyloxytriethylsilane were mixed, metalated, and quenched with acid. Of the four possible products, only **2a** and  $\alpha$ -hydroxy- $\alpha$ -triethylsilyl-*p*-isopropyltoluene, the two corresponding to intramolecular rearrangements, were formed.

It was of interest to determine if alkoxysilanes with  $\alpha$ -carbon atoms bearing protons more acidic than the benzyl protons of **1a** can still undergo rearrangement. Pertinent to this question are the reports by Brook and coworkers<sup>27</sup> of the reaction



(24) See the following papers for further proof.

(25) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 189.

(26) Yu. I. Baukov and I. F. Utsenko, *Organometal. Chem. Rev., Sect. A*, **6**, 355 (1970).

(27) N. V. Schwartz and A. G. Brook, *J. Amer. Chem. Soc.*, **82**, 2439 (1960).

which seems to suggest that the carbanion form of the anion, as written, is the predominant species in solution. Metalation of trimethylsilyloxydiphenylmethane (**1g**) occurs readily, as shown by quenching with  $CH_3I$  which produces **1g** ( $R' = CH_3$ ). Quenching with a proton source, however, produces only recovered **1g** and none of the sought for rearrangement product **2g**. In fact the anion is present in solution in the carbanion form, **1g'**, as shown by the following evidence. First, the anion is deep red in color, showing a strong absorption band at 525 nm. Considering the high dilution required to obtain a spectrum, and the great sensitivity of the anion to moisture, the apparent extinction coefficient of 6,200 is reasonable compared with the reported value of 22,000 for the diphenylmethyl carbanion in diethyl ether,<sup>28</sup> presuming the true value of  $\epsilon$  for both carbanions should not be very dissimilar. Second, the nmr spectrum of the anion of **1g** shows the phenyl proton resonances have been shifted upfield (Table III).<sup>29</sup> Third, methyl iodide reacts very quickly with **1g'**, a rate characteristic of a carbanion not an oxyanion. Also, the red color persists until a full equivalent of methyl iodide is added, showing that this color is not due to a minor carbanion impurity of high basicity. Interesting differences in behavior between silicon and germanium in anionic rearrangements, discussed later in this paper, provide additional evidence for the structure of the anion of **1g**.

The silyl-Wittig rearrangement represents a new synthetic route to  $\alpha$ -silylcarbinols<sup>30</sup> which are difficult to prepare by other methods.<sup>31</sup>

In order to consider properly the thermodynamic factors responsible for the silyl-Wittig rearrangement, the relationship of this rearrangement to the reverse anti-Wittig silyl rearrangement must be resolved. In this latter rearrangement, extensively investigated by Brook, a wide variety of  $\alpha$ -silylcarbinols will rearrange to their isomeric alkoxysilanes in high yield in the presence of *catalytic* quantities of base.<sup>30,9</sup> The rearrangement is known to proceed by an intramolecular pathway, with retention of configuration at silicon, probably through a pentacoordinate silicon intermediate.<sup>32,33</sup> It is thought to be thermodynamically favored by the formation of the strong silicon-oxygen bond in the product. Liquid sodium-potassium alloy, for reasons not fully understood, appears to be a particularly active catalyst for the rearrangement. Hydrogen is not evolved nor is the alloy visibly consumed during rearrangement. Kinetic studies using amine catalysts and para-substituted phenylsilylcarbinols give Hammett reaction constant ( $\rho$ ) values between +3.6 and +4.6, showing the transition state has considerable negative charge dis-

(28) S. F. Mason, *Quart. Rev., Chem. Soc.*, **15**, 336 (1961).

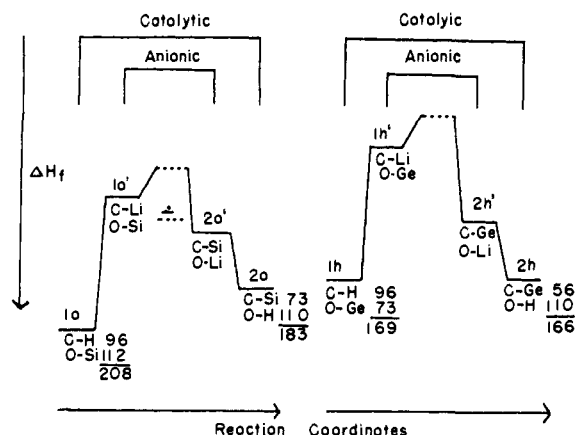
(29) The spectrum is, however, complicated by the presence of **1g** and **3g'** in solution. A conclusive deduction as to anion structure from nmr data is counterbalanced by the eventuality that if the oxyanion form **2g'** were the preferred species in solution, its nmr spectrum, because of restricted rotation of phenyl groups, would probably show a broad multiplet in the phenyl region covering at least some of the region covered by the carbanion isomer **1g'**.

(30) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Amer. Chem. Soc.*, **81**, 981 (1959); G. J. P. Peddle and J. E. H. Ward, *J. Organometal. Chem.*, **13**, 269 (1968).

(31) A. G. Brook, *Advan. Organometal. Chem.*, **6**, 103 (1968).

(32) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

(33) M. S. Biernbaum and H. S. Mosher, *J. Amer. Chem. Soc.*, **93**, 6221 (1971).



**Figure 1.** Energy diagrams for the interconversions of isomers of compounds of the class  $\text{PhCH}_2\text{OMMe}_3$  (**1**) and  $\text{PhCHOMMe}_3$  (**1'**). Approximate thermochemical bond energies are calculated from heats of combustion of simple model compounds:  $E(\text{C-H})\text{CH}_3$  and  $E(\text{O-H})\text{H}_2\text{O}$  from J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968;  $E(\text{Si-O})\text{SiO}_2$ ,  $E(\text{Si-C})\text{Me}_3\text{SiCl}$ , and  $E(\text{Ge-C})\text{Et}_4\text{Ge}$  from E. A. V. Ebsworth in "Organometallic Compounds of Group IV Elements," A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 46;  $E(\text{Ge-O})\text{Ge}(\text{OEt})_4$  from Yu. Kh. Shaulov, A. K. Fedorov, G. Ya. Zueva, G. V. Borisyak, and V. G. Genchel, *Zh. Fiz. Khim.*, **44**, 2081 (1970).

persed into the phenyl ring, consistent with a structure not very different from the carbanion **1'**.

We find that **2a** undergoes such a rearrangement, when treated 10 sec with sodium-potassium alloy in THF at  $25^\circ$ , to produce 92% **1a**. Even **2a'** itself, if present in only catalytic amounts, will isomerize **2a** to **1a**, 86% rearrangement occurring in 25 hr at  $25^\circ$  in THF solution. This is in contrast to the situation when one full equivalent of anion is present. As we have seen, **1a**, metalated in THF with excess lithium diisopropylamide at  $25^\circ$ , or **2a**, totally converted to **2a'** with 1 equiv of *n*-butyllithium in THF, both give only **2a** and no **1a** upon acidification, regardless of the time the anion solution is let stand at  $25^\circ$ .

It is of interest to consider the reason for the different thermodynamics of the catalytic and full anion equivalent isomerizations. Figure 1 shows qualitatively the relative heats of formation of the species involved, consistent both with the experimental results and the known approximate thermochemical bond energies of the bonds made and broken in the isomerizations. In the catalytic rearrangement, the neutral species **2a** and **1a** are being equilibrated, and the high strength of the Si-O bond relative to the Si-C bond results in the sum of the Si-O and PhC-H bond energies in **1a** exceeding the sum of the C-Si and OH bond energies in **2a**. The equilibrium must therefore lie toward **1a**. When one full equivalent of anion is present, the thermodynamic equilibrium is between the anions **1a'** and **2a'**, and it is apparent that the stabilization energy gained in having the negative charge located on oxygen as in **2a'** rather than on carbon as in **1a'** outweighs the energy lost by placing the silicon on carbon rather than on oxygen. Quantitatively, if the  $\text{p}K_a$  of **1a** is 35 and the  $\text{p}K_a$  of **2a** is 17,<sup>21</sup> the transition **1a**  $\rightarrow$  **1a'** requires excess energy over the transition **2a**  $\rightarrow$  **2a'** of 25 kcal/mol at  $25^\circ$ . From Figure 1 it is seen that the transition **1a**  $\rightarrow$  **2a** also requires 25 kcal/mol (208-183). This would leave **1a'** with the same energy as **2a'**, not in ac-

cord with the experimental results. The discrepancy may lie in the inherent uncertainty of either the values of the thermochemical bond energies given in Figure 1 or in the  $\text{p}K_a$  values used. If the energy difference in the transition **1a**  $\rightarrow$  **2a** were less than 25 kcal/mol, the preference of anion **2a'** over **1a'** would be accounted for. Presumably the function of **2a'** when used as a catalyst for the isomerization of **2a** to **1a** is to provide a minute equilibrium amount of **1a'** or a related species which is then irreversibly protonated by a carbinol proton of **2a** to form **1a**.

In the anion rearrangement of the siloxydiphenylmethane **1g**, the higher acidity of the benzhydryl proton reduces the energy of the transition **1g**  $\rightarrow$  **1g'**, leaving **1g'** more stable than **2g'**.

**(b) Germanium-Oxygen Rearrangements.** Whereas the catalytic Brook rearrangement of  $\alpha$ -silylcarbinols to alkoxygermanes appears to be quite general, the only reported case of a catalytic rearrangement of an  $\alpha$ -germylcarbinol to an alkoxygermane is that of 9-triphenylgermyl-9-fluorene to 9-triphenylgermyloxyfluorene, an isomerization thought not to be general.<sup>34</sup>

Of particular interest then is the possibility of isomerizing in the reverse direction the anion of benzyl-oxytrimethylgermane **1h'** to **2h'** in the presence of excess base. Metalation of **1h** in THF with excess tert-butylolithium at  $-78^\circ$  gives an almost colorless solution. Protonating the anions present 10 min after tert-butylolithium addition gives **2h** in 70% yield and benzyl alcohol in 30% yield. The absence of **1h** as a product indicates that metalation and subsequent rearrangement are fast. **1h** is not hydrolyzed to benzyl alcohol under the conditions of work-up. This represents the first example of a 1,2-anionic rearrangement from oxygen to an  $\alpha$  carbanion in which germanium is the migrating group.

Since rearrangement is fast, it appears that the migration of germanium from oxygen to carbon occurs through a transition state of energy not much greater than the energy of carbanion **1h'**. This suggests that germanium, like silicon, can form low-energy penta-coordinate transition states in 1,2-anionic rearrangements.<sup>35</sup>

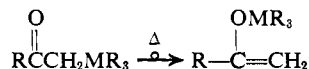
The nmr of the anion solution prepared from **1h** shows only one trimethylgermyl resonance (other than that of the side product tert-butyltrimethylgermane); the phenyl resonance at  $\tau$  2.81 suggests the anion is in the oxyanion form **2h'** (Table III). Contrary to our silicon example, **1a**, the anion of **1h** reacts slowly with methyl iodide giving only the rearranged isomer **2h** ( $\text{R}'' = \text{CH}_3$ ), showing the anion to be entirely in the form **2h'**. Since the C-Li bond energy in the germane **1h'** and the O-Li bond energy in **2h'** should be almost the same as these respective bond energies in **1a'** and **2a'**, the above result seems to indicate that the difference  $E(\text{Ge-O}) - E(\text{Ge-C})$  is less than the difference  $E(\text{Si-O}) - E(\text{Si-C})$  (Figure 1). The approximate literature values for model compounds,  $73 - 56 = 17$  kcal for germanium and  $112 - 73 = 39$  kcal for silicon, support this conclusion.

(34) G. J. D. Peddle and J. E. H. Ward, *J. Organometal. Chem.*, **14**, 131 (1968), and references therein.

(35) Although germanium reportedly uses empty 3d orbitals to a lesser extent than silicon in bonding, germanium expands its coordination sphere from four to six more easily.<sup>20</sup> Apparently the second effect at least counterbalances the first in our example.

It would be of considerable interest to see if the above conclusion regarding energy differences in similar silicon and germanium isomerizations applies to the isomerization of the anion of trimethylgermyloxydiphenylmethane (**1j**). Since we have shown the anion of trimethylsilyloxydiphenylmethane (**1g**) to exist in the unusual carbanion form **1g'**, the existence of the anion of **1j** in the opposite oxyanion form **2j'** would vindicate that conclusion. It has been reported that triphenylgermyllithium adds normally to benzophenone to give a carbinol, not an alkoxygermane.<sup>36</sup> Studying the metalation of **1j** would suggest whether this product had been kinetically or thermodynamically favored in its formation. In fact metalation of **1j** occurred readily under the same reaction conditions used for **1g**. Dramatically, quenching with a proton source produces the *rearranged* isomer **2j** and no recovered **1j'**. The anion, furthermore, appears to be in the *oxyanion* form, **2j'**, in solution. The anion is colorless, unlike the silicon analog which is red. The nmr spectrum of the anion shows a broad multiplet between  $\tau$  2.46 and 3.16, similar to that of **2j** which occurs between  $\tau$  2.30 and 3.02. The most convincing evidence, however, is the result that contrary to the behavior of the analogous silicon anion methyl iodide reacts only slowly with the anion to produce the *rearranged* isomer **2j** ( $R'' = \text{CH}_3$ ), an amazing result showing there is *little or no carbanion species, 1j'*, present.

There are additional chemical differences between silicon and germanium reported in the literature, consistent with the observed absence of a general germanium Brook rearrangement. Thus, benzylgermanes are cleaved by alcoholic sodium hydroxide  $10^3$  times slower than are benzylsilanes.<sup>37</sup> These reactions are significant since here metalloid-carbon bonds are replaced by metalloid-oxygen bonds as in the Brook rearrangement. Of interest also is the fact that the following ketone to enol thermal rearrangement occurs for silicon- but not for germanium-substituted ketones.<sup>38,39</sup>



Literature bond energies predict **1h** to be thermodynamically slightly more stable than **2h** (Figure 1). The absence of the catalytic rearrangement of **2h** to **1h** might mean that these bond energy values are not exactly correct for this system and that actually **2h** is thermodynamically preferred. On the other hand, an inaccessible transition state could also be responsible for the lack of catalytic rearrangement. We have seen, from the results of methyl iodide quenching in the anion rearrangement, that the high energy of transition **2h'**  $\rightarrow$  **1h'** prevents any detectable amount of **1h'** from being present at equilibrium. In the unknown catalytic rearrangement of **2h**, if the lowest pathway available in base or alkali metal catalysis would involve a transition state not very different than carbanion **1h'** in structure and energy, then it appears likely that this transition state, like **1h'**, would also be inaccessible from **2h'** (or **2h**), thus preventing rearrangement for kinetic reasons.

(36) D. A. Nicholson and A. L. Allred, *Inorg. Chem.*, **4**, 1751 (1965).

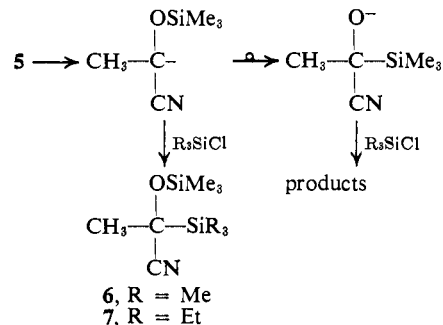
(37) R. W. Bott and C. Eaborn, *J. Chem. Soc.*, 2342 (1963).

(38) A. G. Brook, D. M. McRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, **89**, 5493 (1967).

(39) I. F. Lutsenko, Yu. I. Baukov, D. V. Dudukina, and E. N. Kramarona, *J. Organometal. Chem.*, **11**, 35 (1968).

## Metalation of Silyl Cyanohydrins

The metalation of acetal-protected cyanohydrins  $\alpha$  to cyanide for use as acyl carbanion equivalents<sup>40</sup> in synthesis has recently been reported.<sup>41</sup> Treatment of monolithiated acetonitrile with trimethylchlorosilane yields trimethylsilylacetonitrile.<sup>42</sup> The possibility of effecting the metalation and rearrangement of a trimethylsilyl-protected cyanohydrin was therefore investigated.



2-Trimethylsilyloxypropionitrile, **5**, prepared by silylating acetaldehyde cyanohydrin, is metalated at  $-78^\circ$  with lithium diisopropylamide in tetrahydrofuran. Quenching after 15 min with trimethylchlorosilane yields **6** in about 15% yield and several inseparable unstable high molecular weight products containing the trimethylsilyl group and showing a carbonyl but no CN or silylcarbonyl stretch in the ir. In a separate experiment quenching after 15 min with triethylchlorosilane yields 30% **7**.

That rearrangement had not occurred in the formation of **7** was evidenced by the trimethylsilyl resonance at  $\tau$  9.78 which corresponded exactly to the chemical shift of the trimethylsilyloxy resonance in **5** and to the more downfield trimethylsilyl resonance in **6** and which therefore suggested the trimethylsilyl group in **7** was still attached to oxygen. The formation of the trimethylsilylated by-products likely occurred through migration of silicon from oxygen to the neighboring carbanion, elimination of cyanide anion, and decomposition of the resulting  $\alpha$ -silyl ketone.

## Experimental Section

All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were recorded on Varian A-60 and JEOL MH-100 spectrometers. Gas-liquid chromatographic (glc) separations were made on a Varian Aerograph A-700 chromatograph using columns packed with either SE-30 or QF-1 silicone on Chromosorb W. Mass spectra were obtained using an AIE Model MS-9 spectrometer. All boiling points and melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-33 spectrometer.

Reaction product mixtures were purified by distillation and then resolved into individual pure compounds by preparative glc. Reported product distributions are based on relative glc peak areas confirmed, where possible, by nmr analysis of crude reaction mixtures. Unless otherwise noted, distillations were completed with less than ca. 10% residue remaining in the stillpot.

*tert*-Butyllithium, 1.27 M in pentane, and *n*-butyllithium, 1.6 M in hexane, were obtained inexpensively in 1-gallon cylinders from Foote Mineral Co., New Johnsonville, Tenn. Tetrahydrofuran

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(41) G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971).

(42) G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **93**, 1714 (1971).



solution then recooled to  $-78^\circ$ . The homogeneous solution was pale yellow, the same color as a solution of THF and tertiarybutyllithium alone treated in the same way. The nmr of the anion at  $-78^\circ$  was recorded. A small peak at  $\tau$  12.07 suggested the presence of a few per cent of Si-CH<sub>2</sub>Li species. After 2 min at  $-78^\circ$ , 59 ml (30 mmol) of the anion solution was transferred at  $-78^\circ$  to a 100-ml flask and quenched with 20 ml of a 1:1 THF-glacial acetic acid solution. After removing lithium acetate by extracting with 20 ml of water, solvent removal and vacuum distillation afforded 5.0 g (93%) of an oil consisting of 95 parts rearranged isomer **2a**, 1 part benzyl alcohol, and 4 parts **1a**, according to glc and nmr analysis.

A second 59-ml portion of the anion was injected into 4.5 g (30 mmol) of triethylchlorosilane in 20 ml of THF at  $-78^\circ$ . Derivatization occurred upon warming to  $25^\circ$ . Anhydrous work-up gave 7.2 g (82%) of an oil consisting of 96 parts **2a** ( $R'' = Et_3Si$ ), 2 parts benzyloxytriethylsilane, and 2 parts **4a** ( $R'' = Et_2Si$ ).

A third 59-ml portion of the anion was injected into 4.2 g (30 mmol) of methyl iodide in 20 ml of THF at  $-78^\circ$ . Derivatization occurred slowly over a 20-min period at  $25^\circ$  to give, upon anhydrous work-up, 3.9 g (67%) of an oil consisting of 91 parts 1-phenyl-1-trimethylsilyloxyethane<sup>44</sup> (**1e**), 7 parts  $\alpha$ -methoxy- $\alpha$ -trimethylsilyltoluene (**2a**,  $R'' = Me$ ), 1 part benzyl methyl ether, and 1 part of an unknown compound, possibly benzyloxydimethylethylsilane (**4a**,  $R'' = Me$ ). **1e**: nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.76 (s, 5, Ph), 5.18 (q, 1, CHCH<sub>3</sub>,  $J = 6$  Hz), 8.60 (d, 3, CHCH<sub>3</sub>,  $J = 6$  Hz), 9.97 (s, 9, SiMe<sub>3</sub>). **2a** ( $R'' = Me$ ):  $n^{20D}$  1.4900; ir (neat) 1250 cm<sup>-1</sup> (Me<sub>3</sub>Si); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.88 (s, 5, Ph), 6.08 (s, 1, CH), 6.75 (s, 3, OCH<sub>3</sub>), 10.06 (s, 9, SiMe<sub>3</sub>).

Anal. Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>Si: C, 67.98; H, 9.34; Si, 14.45. Found: C, 68.28; H, 9.35; Si, 14.32.

The remaining 59-ml portion of anion was injected into 3.7 g (30 mmol) of methyl sulfate in 20 ml of THF at  $-78^\circ$ . Derivatization apparently occurred rapidly. Anhydrous work-up gave the products listed in Table I.

**Rearrangement of Benzyloxytriethylsilane (1b).** Protonating the anion solutions (Table I) gave mainly  $\alpha$ -hydroxy- $\alpha$ -triethylsilyltoluene (**2b**): bp 140° (0.03 Torr);  $n^{20D}$  1.5164; ir (neat) 3200–3650 cm<sup>-1</sup> (OH); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.84 (s, 5, Ph), 5.45 (s, 1, CH), 8.30 (s, 1, OH), 8.9–9.8 (m, 15, SiEt<sub>3</sub>).

Anal. Calcd for C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>Si: C, 70.24; H, 9.98; Si, 12.63. Found: C, 70.08; H, 9.93; Si, 12.45.

Derivatizing the anion solution of **1b** in THF with Me<sub>3</sub>SiCl gave only  $\alpha$ -trimethylsilyloxy- $\alpha$ -triethylsilyltoluene (**2b**,  $R'' = Me_3Si$ ), identified from its nmr spectrum and from the fact that acid hydrolysis gave **2b** on work-up. Derivatizing the anion solution of **1b** in THF with methyl iodide gave mainly 1-phenyl-1-triethylsilyloxyethane (**1b**,  $R'' = CH_3$ ): nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.84 (s, 5, Ph), 5.25 (q, 1,  $J = 6$  Hz, CH-CH<sub>3</sub>), 8.68 (d, 3,  $J = 6$  Hz, CH-CH<sub>3</sub>), 9.00–9.85 (m, 15, SiEt<sub>3</sub>). Quenching with methyl sulfate gave predominantly  $\alpha$ -methoxy- $\alpha$ -triethylsilyltoluene (**2b**,  $R'' = Me$ ): nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.90 (s, 5, Ph), 6.11 (s, 1, CH), 6.82 (s, 3, OCH<sub>3</sub>), 9.00–9.85 SiEt<sub>3</sub>).

**Rearrangement of Benzyloxytertiarybutyldimethylsilane (1c).** Protonating the anion solutions gave mainly  $\alpha$ -hydroxy- $\alpha$ -tertiarybutyldimethylsilyltoluene (**2c**): bp 86° (0.10 Torr); mp 28°; ir (neat) 3450 (OH) and 1250 cm<sup>-1</sup> (SiMe<sub>3</sub>); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.87 (s, 5, Ph), 5.48 (s, 1, CH), 8.40 (s, 1, OH), 9.04 (s, 9, *t*-Bu), 10.05 (s, 3, SiCH<sub>3</sub>), 10.23 (s, 3, SiCH<sub>3</sub>).

Anal. Calcd for C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>Si: C, 70.24; H, 9.98; Si, 12.63. Found: C, 70.34; H, 9.85; Si, 12.78.

**Rearrangement of Benzyloxytriphenylsilane (1d).** Protonating an anion solution of **1d** (4.7 g, 12.8 mmol) formed in THF gave 8.2 g (50%) of  $\alpha$ -hydroxy- $\alpha$ -triphenylsilyltoluene (**2d**): mp 114° (lit.<sup>45</sup> mp 116–117°); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.75–3.07 (m, 20, Ph), 4.92 (s, 1, CH), 8.21 (s, 1, OH). Nmr analysis of a sample of retained crude reaction mixture showed 6% **1d**, 7% benzyl alcohol, 61% **2d**, and 26% unidentified materials to be present.

**Rearrangement of 1-Phenyl-1-trimethylsilyloxyethane (1e).** Protonating an anion solution of **1e** (9.7 g, 50 mmol) formed in THF with a twofold excess of *tert*-butyllithium gave 7.3 g (75%) of an oil which by glc analysis consisted of 5 parts **1e**, 56 parts 1-phenylethanol, 29 parts unknown "A," and 10 parts unknown "B." Preparative glc showed "A" to be 1-phenyl-1-trimethylsilyloxyethanol (**2e**):  $n^{20D}$  1.5151; ir (neat) 3450 (OH) and 1250 cm<sup>-1</sup> (SiMe<sub>3</sub>); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.83 (s, 5, Ph), 8.45 (s, 3, CH<sub>3</sub>), 8.73 (s, 1, OH), 10.03 (s, 9, SiMe<sub>3</sub>).

Anal. Calcd for C<sub>11</sub>H<sub>18</sub>SiO: C, 67.98; H, 9.34. Found: C, 67.36; H, 9.07.

"B" was 1-(trimethylsilylphenyl)ethanol, Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CHCH<sub>3</sub>OH: mp 61°; ir (neat) 3350 (OH) and 1250 cm<sup>-1</sup> (SiMe<sub>3</sub>); nmr (CCl<sub>4</sub>,

TMS)  $\tau$  2.74 (m, 4, C<sub>6</sub>H<sub>4</sub>), 5.87 (q, 1,  $J = 6.4$  Hz, CHCH<sub>3</sub>), 7.56 (s, 1, OH), 8.70 (d, 3,  $J = 6.4$  Hz, CHCH<sub>3</sub>), 9.68 (s, 9, SiMe<sub>3</sub>).

**Metalation of Trimethylsilyloxydiphenylmethane (1g).** *tert*-Butyllithium (10 ml, 12 mmol) was added to **1g** (2 g, 8 mmol) in 10 ml of THF at  $-78^\circ$ . A deep red color slowly developed. The nmr and uv spectra of the anion solution were recorded. After 2 hr at  $-20^\circ$  the anion was quenched with acetic acid-THF. On work-up of the resulting colorless solution, only **1g** and diphenylcarbinol were recovered. Repeating the reaction using DCl in D<sub>2</sub>O to quench gave **1g**, 77% monodeuterated at the phenyl-substituted carbon according to nmr analysis. A new sample of anion was quenched with methyl iodide. Reaction was rapid. The deep red color persisted until 8 mmol of CH<sub>3</sub>I had been added. Work-up gave 2.0 g (94%) of an oil consisting of 13 parts recovered **1g**, 12 parts methoxydiphenylmethane, and 75 parts 1-trimethylsilyloxy-1,1-diphenylethane (**1g**,  $R'' = CH_3$ ):  $n^{20D}$  1.5395; ir (neat) 1250 cm<sup>-1</sup> (Me<sub>3</sub>Si); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.80 (m, 10, Ph<sub>2</sub>C), 8.1 (s, 3, CH<sub>3</sub>), 10.02 (s, 9, SiMe<sub>3</sub>).

Anal. Calcd for C<sub>17</sub>H<sub>22</sub>SiO: C, 75.50; H, 8.20; Si, 10.38. Found: C, 76.41; H, 8.20; Si, 10.56.

The deviation in carbon analysis may result from slight decomposition on gas chromatography. This compound hydrolyzed in ethanol-H<sub>2</sub>O-HCl to give diphenylmethylcarbinol, according to nmr analysis. The anion **1g'** did not react with triethylchlorosilane, even at 47°.

**Rearrangement of Benzyloxytrimethylgermane (1h).** Protonating an anion solution of **1h** (300 mg, 1.33 mmol), formed in THF using *tert*-butyllithium gave, upon work-up, 29 parts benzyl alcohol and 71 parts  $\alpha$ -hydroxy- $\alpha$ -trimethylgermyltoluene (**2h**):  $n^{20D}$  1.5268; ir (neat) 3360 cm<sup>-1</sup> (OH); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.90 (s, 5, Ph), 5.42 (s, 1, PhCH), 7.97 (s, 1, OH), 9.92 (s, 9, GeMe<sub>3</sub>). The mass spectrum gave a molecular ion at 226 for <sup>74</sup>Ge, the isotopic distribution being correct for the presence of one germanium atom.

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>GeO: C, 53.42; H, 7.17. Found: C, 52.62; H, 6.98.

A new sample of anion was quenched with methyl iodide yielding an oil consisting of 17 parts methyl benzyl ether and 83 parts  $\alpha$ -methoxy- $\alpha$ -trimethylgermyltoluene:  $n^{20D}$  1.5830; ir (neat) 1170 (OCH<sub>3</sub>); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.89 (m, 5, Ph), 5.92 (s, 1, PhCH), 6.76 (s, 3, OCH<sub>3</sub>), 9.94 (s, 9, GeMe<sub>3</sub>).

Anal. Calcd for C<sub>16</sub>H<sub>26</sub>GeO: C, 55.21; H, 7.60. Found: C, 55.07; H, 7.64.

**Rearrangement of Trimethylgermyloxydiphenylmethane (1j).** **1j** (2.0 g, 6.7 mmol) was metalated using the exact procedure given for **1g**. One-half the pale red anion was quenched with acetic acid-THF. Work-up of the colorless solution gave 0.80 g (80%) of an oil consisting of 30 parts diphenylcarbinol and 70 parts trimethylgermyloxydiphenylmethanol (**2j**), which could not be obtained in over 90% purity, due to decomposition in the chromatograph: ir (neat) 3470 cm<sup>-1</sup> (OH); nmr (CCl<sub>4</sub>, TMS), impurities subtracted  $\tau$  2.29–3.04 (m, 10, Ph<sub>2</sub>C), 7.91 (s, 1, OH), 9.82 (s, 9, GeMe<sub>3</sub>). The mass spectrum gave the correct molecular ion isotope pattern for one germanium atom, M<sup>+</sup> (Ge<sup>74</sup>) 302.

The other half of the anion was quenched with methyl iodide. The pale red color immediately disappeared after only 0.3 mmol of CH<sub>3</sub>I had been added. Glc analysis showed reaction was slow, 16 hr at 25° being required. Work-up gave 0.73 g (73%) of an oil consisting of 27 parts methoxydiphenylmethane, 11 parts **2j**, and 62 parts trimethylgermyloxydiphenylmethoxymethane (**2j**,  $R'' = CH_3$ ):  $n^{20D}$  1.5722; nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.84 (s, 10, Ph<sub>2</sub>C), 6.90 (s, 3, OCH<sub>3</sub>), 9.84 (s, 9, GeMe<sub>3</sub>).

Anal. Calcd for C<sub>17</sub>H<sub>22</sub>GeO: C, 64.81; H, 7.04. Found: C, 65.00; H, 6.77.

This compound could not be hydrolyzed in ethanol-H<sub>2</sub>O-HCl. Therefore the structure assigned is that of the correct isomer.

**Rearrangements with Lithium Diisopropylamide. General Procedure.** *n*-Butyllithium solution (15 ml, 24 mmol) was added to 2.4 g (24 mmol) of diisopropylamide in 15 ml of THF at  $-78^\circ$ . Alkoxyasilane or alkylthiosilane (16 mmol) was then added. After holding the solution at the temperature and for the time listed in Table II, glacial acetic acid in THF was injected at  $-78^\circ$ , the salts were washed out with water, and the solvent was evaporated from the organic layer. The resultant oils were analyzed by glc. The results are tabulated in Table I.

**Mixing Experiment.** *tert*-Butyllithium (29 ml, 36 mmol) was added to a flask containing *p*-isopropylbenzyloxytriethylsilane (3.6 g, 14 mmol) and benzyloxytrimethylsilane (**1a**) (2.5 g, 14 mmol) frozen in THF at  $-196^\circ$ . The solution was warmed from  $-78$  to  $-30^\circ$  over a 2-hr period and quenched with acetic acid in THF. Work-up gave 5.7 g (85%) of an oil consisting of 1 part **1a**, 49 parts



**2a**, 2 parts recovered *p*-isopropylbenzyloxytriethylsilane, and 48 parts  $\alpha$ -hydroxy- $\alpha$ -triethylsilyl-*p*-isopropyltoluene: nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.96 (s, 4, C<sub>6</sub>H<sub>4</sub>), 5.53 (s, 1, PhCH), 7.17 (septet, 1, *J* = 7 Hz, Me<sub>2</sub>CH), 8.31 (s, 1, OH), 8.76 (d, 6, *J* = 7 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 8.8–9.6 (m, 15, SiEt<sub>3</sub>).

**Metalation of 2-Trimethylsiloxypropionitrile (5).** *n*-Butyllithium (23.8 ml, 38.1 mmol) was added to diisopropylamine (3.85 g, 38.1 mmol) in 24 ml of THF at  $-78^\circ$ . **5** (3.62 g, 25.4 mmol) was then added, followed, after 15 min, by triethylchlorosilane (5.7 g, 38.1 mmol). The solution was warmed to  $25^\circ$ . Anhydrous work-up

gave 4.02 g of an oil, containing 62% of 2-trimethylsiloxy-2-triethylsilylpropionitrile (**7**): bp  $70^\circ$  (0.13 Torr);  $n_D^{20}$  1.5536; ir (neat) 2240 (C $\equiv$ N) and 1250 cm<sup>-1</sup> (Me<sub>3</sub>Si); nmr (CCl<sub>4</sub>, TMS)  $\tau$  8.66 (s, 3, CCH<sub>3</sub>), 7.6–8.9 (m, 15, SiEt<sub>3</sub>), 9.78 (s, 9, OSiMe<sub>3</sub>).

*Anal.* Calcd for C<sub>12</sub>H<sub>27</sub>NOSi<sub>2</sub>: C, 56.50; H, 10.67; Si, 22.00. Found: C, 57.08; H, 10.69; Si, 21.28.

Repeating the reaction, derivatizing with trimethylchlorosilane gave 15% 2-trimethylsiloxy-2-trimethylsilylpropionitrile (**6**): ir (neat) 2230 (C $\equiv$ N) and 1250 cm<sup>-1</sup> (Me<sub>3</sub>Si); nmr (CCl<sub>4</sub>, TMS)  $\tau$  8.65 (s, 3, CCH<sub>3</sub>), 9.78 (s, 9, OSiMe<sub>3</sub>), 9.84 (s, 9, SiMe<sub>3</sub>).

## New Anionic Rearrangements. XVIII. 1,2-Anionic Rearrangements from Sulfur to Carbon in Benzylthiotrimethylsilane and Benzylthiotrimethylgermane<sup>1,2</sup>

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**Abstract:** Benzylthiotrimethylsilane (**1a**) and benzylthiotrimethylgermane (**1b**), upon metalation at the benzyl carbon atom with excess *tert*-butyllithium or lithium diisopropylamide in tetrahydrofuran, rearrange rapidly *via* 1,2-shift of silicon or germanium to the  $\alpha$  carbanion to give, in high yield, anions of  $\alpha$ -mercapto- $\alpha$ -trimethylsilyltoluene (**2a**) and  $\alpha$ -mercapto- $\alpha$ -trimethylgermyltoluene (**2b**), respectively. These anions can be protonated, alkylated, or silylated at sulfur. **2a** and **2b** rearrange spontaneously at  $195^\circ$ , or at  $100^\circ$  in the presence of catalytic amounts of radical initiator, to **1a** and **1b**, respectively, in high yield. In this novel catalytic rearrangement, the neutral species **1a** and **1b** are thermodynamically favored over **2a** and **2b**. In the anion rearrangement, the equilibrium is between anions, and the stability gained by placing the negative charge on sulfur, rather than on carbon, makes the anions of **2a** and **2b** the favored isomers at equilibrium. Methylthio-*tert*-butyldimethylsilane, upon metalation, rearranges to *tert*-butyldimethylsilylmethanethiol.

In the previous paper we reported that benzyloxytrimethylsilane, upon metalation at the benzyl carbon atom with excess *tert*-butyllithium, rearranges rapidly and in high yield *via* 1,2-shift of silicon from oxygen to the  $\alpha$  carbanion to give the anion of  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**1c'**  $\rightarrow$  **2c'**, Scheme I). The analogous germanium rearrangement, **1d'**  $\rightarrow$  **2d'**, was also described.

In searching for new examples of 1,2-anionic silicon and germanium rearrangements, the sulfur analogs of **1c** and **1d**, benzylthiotrimethylsilane (**1a**) and benzylthiotrimethylgermane (**1b**), were considered. If these molecules could be selectively metalated at the benzyl carbon atoms, migration of silicon or germanium from sulfur to the  $\alpha$  carbanion might occur. The weak silicon-sulfur bond in **1a'**, and the weakly basic sulfur anion in **2a'**, could be expected to make the isomerization **1a'**  $\rightarrow$  **2a'** even more thermodynamically favored than the analogous isomerization of the oxygen species **1c'**  $\rightarrow$  **2c'**.

The counterpart to the alkoxy silane to silylcarbinol rearrangement **1c'**  $\rightarrow$  **2c'** in organic chemistry is the well known Wittig rearrangement of a metalated ether to its isomeric alcohol.<sup>4,5</sup> As discussed previously,<sup>2</sup>

migration of carbon from oxygen to the carbanion is slow.<sup>6</sup> When silicon migrates, rearrangement can be fast, because silicon may become pentacoordinate in the transition state,<sup>7</sup> removing the symmetry restrictions<sup>8</sup> to rearrangement present in the Wittig rearrangement.<sup>9</sup>

The counterpart to the silicon-sulfur rearrangement **1a'**  $\rightarrow$  **2a'** in organic chemistry would be the isomerization of a metalated organic sulfide to a mercaptide anion, in which migration of carbon from sulfur to an  $\alpha$  carbanion would occur. This process is not observed; metalation of the rather acidic proton  $\alpha$  to sulfur in sulfides,<sup>10</sup> sulfoxides,<sup>16</sup> and sulfones<sup>17</sup> commonly pro-

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