Oxasilocins from Fluoride Ion Induced Ring Expansion

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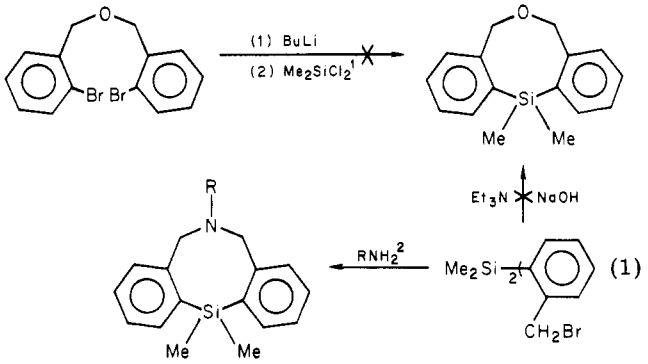
Reaction of fluoride ion sources with 11-(halomethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*][1,4]oxasilepin generates isomers of 11-methyl-11-fluoro-11,12-dihydro-6*H*-dibenzo[*b*,*f*]oxasilocins. Maximum conversion of silepin to silocins occurs from the iodomethyl precursor and a slight stoichiometric excess of tetrabutylammonium fluoride. The oxasilocins are cleaved by excess fluoride ion to the ethers, benzyl *o*-tolyl ether and phenyl *o*-xylyl ether, and reduced with lithium aluminum hydride to the corresponding 11-methyldibenzo[*b*,*f*]oxasilocins. The spectroscopic properties of this new heterocyclic system are described.

Introduction

The routes to medium-sized rings which contain silicon heteroatoms are few. The two tactics in general use include the reaction of a dilithio or diGrignard reagent with an organosilicon dihalide or by ring closure through reaction of an appropriate carbofunctional organosilane. The Grignard route is not useful when the size of the ring formed in the reaction process is larger than seven atoms. The failure of these two general approaches in attempts to form dibenzo[*c*,*f*][1,5]oxasilocins has been previously reported (eq 1),[1] although the related azasilocins may be formed from bis(*o*-(bromomethyl)phenyl)dimethylsilane and primary amines.[2]

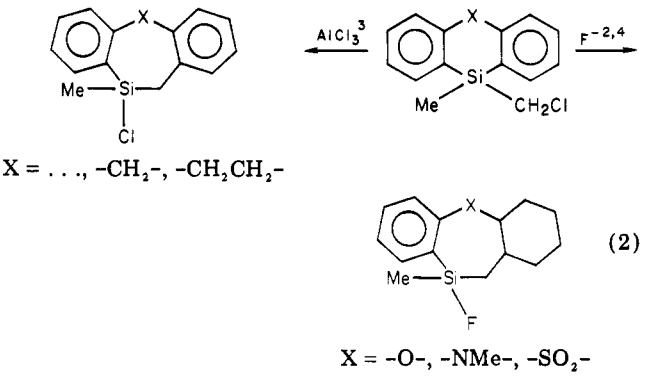


A third approach to medium-sized rings is through ring expansion. Dibenzo[*b*,*f*]silocins are formed in reasonable yields from the appropriate dibenzo[*b*,*f*]silepin precursor and aluminum chloride (eq 2), but acid catalysts are not effective for silacycles which contain heteroatoms with lone electron pairs. Dibenzoheterosilepins are generated from phenheterosilins on reaction with stoichiometric fluoride (eq 2).

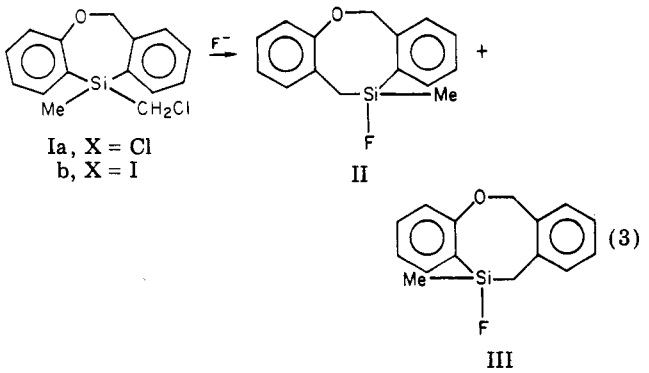
The present study describes the results of the fluoride ion induced reactions of 11-(halomethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*][1,4]oxasilepins which lead to the formation of isomers of the dibenzo[*b*,*f*]oxasilocin system.

Results and Discussion

The fluoride ion induced reaction of a dibenzo[*b*,*e*]-[1,4]oxasilepin could lead to two isomers of dibenzo[*b*,*f*]-



oxasilocin (eq 3). Initial efforts focused on the conditions



which had previously proved successful for the conversion of six-membered rings to seven-membered rings (eq 2). No reaction was observed between Ia and KF·HF in refluxing acetonitrile after 20 h, and with addition of 18-crown-6 only minor reaction occurred after 22 h. With KF(tech), reaction also was slow but, when 18-crown-6 was added, no starting material was observed after 24 h (KF/Ia = 1.5). The product mixture that was obtained contained the silocin as a minor component. When the relative molar amount of KF(tech) and the reflux period were both decreased, the yield of silocin increased but starting material was still present. The preliminary studies also showed that the volatile reaction products contained only one silocin isomer as well as ethers that would be formed from cleavage of the ring-expanded products (eq 4 and 5). For verification of this assignment, authentic samples of IV and V were prepared from *o*-cresol/α-bromotoluene[5] and phenol/*o*-methylbenzyl bromide, respectively.

(1) Chang, V. H. T.; Corey, J. Y. *J. Organomet. Chem.* **1980**, *190*, 217.
(2) Corey, J. Y.; Janoski, H. M.; Vermont, D. F.; Paton, J. P.; Chang, V. H. T. *J. Organomet. Chem.* **1980**, *194*, 15.
(3) Corey, J. Y.; Francis, E. A.; Bursten, M. S.; Kunz, J. C. *J. Organomet. Chem.* **1981**, *210*, 149.
(4) Corey, J. Y.; Chang, V. H. T. *J. Organomet. Chem.* **1979**, *174*, C15.
(5) Curtin, D. Y.; Wilhelm, M. *J. Org. Chem.* **1958**, *23*, 9.

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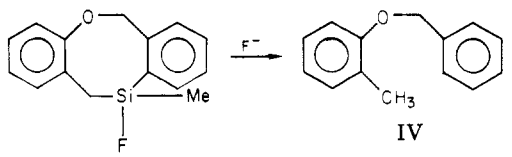

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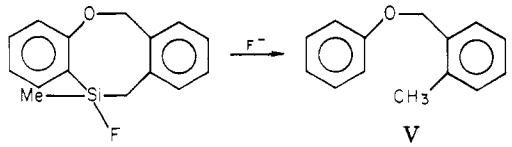
IV



(5)

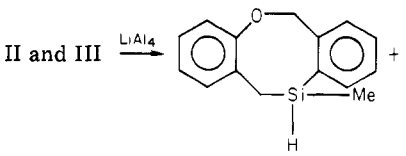
V

In an effort to improve conversion of Ia to the silocin other conditions were explored. The formation of IV and V suggests that both the starting silepin and the silocin product compete for the fluoride ion and thus an excess of fluoride should be avoided. When the ratio of F^-/Ia is decreased, the amount of silocin isolated is higher. If cleavage of silocins occurs more slowly than expansion of the silepin, then an approach designed to increase the rate of conversion of silepin when close to the stoichiometric quantity of F^- is present should improve the yields of silocins. The homogeneous conditions provided by $Bu_4N^+F^-$/THF result in a higher proportion of product isolated as silocin although the yields of II, III, IV, and V combined do not alter significantly. An alternative to homogeneous conditions was found in the combination of KF and KI (KF/KI = 10). The rate of conversion of Ia to Ib occurs faster than Ia to II or III, and in general, iodomethyl derivatives undergo ring expansion more rapidly than the chloromethyl derivatives.[3] Again, the percent of the combination of II through V is not significantly different from that achieved with KF/crown, but the silocin is the major product. With either $Bu_4N^+F^-$/THF or KF/KI only one silocin isomer appears to be formed in the time that Ia is consumed.

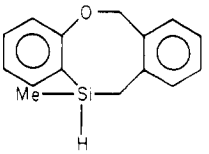
The reaction of the iodomethyl derivative, Ib, occurs with excess KF within 10 h in the absence of crown ether. When close to the stoichiometric amount of KF is employed, the product mixture contains both silocin isomers and minimal or no detectable cleavage-derived ethers. The two silocin isomers are formed in about a 2/1 ratio, with the major isomer identical with the silocin isolated from reactions of Ia. The use of $Bu^4N^+F^-$/THF also provides both silocins and no detectable cleavage-derived ethers although a minor component (~5%) of the product mixture contains what appears to be *o*-($MeSiH_2$)$C_6H_4OCH_2C_6H_4CH_3$-*o* or its isomer. The yield of silocin products exceeds 60% when Ib is used under homogeneous conditions.

The structure of the major isomer from the reaction of Ib and of the only isomer obtained from Ia was determined by reaction of isolated, purified samples of both silocin products with KF. The minor isomer reacts completely with KF(tech) in less than 18 h in refluxing CH_3CN to give *o*-$CH_3C_6H_4CH_2OC_6H_5$, V, as the major product as determined by ^1H NMR. These results are consistent with the silocin III as the minor isomer. The major silocin isomer shows no detectable reaction with KF(tech) after 24 h in refluxing acetonitrile. Addition of crown ether was required to convert the major isomer to *o*-$CH_3C_6H_4OCH_2C_6H_5$, IV, as the only identifiable product (91%). Authentic samples of IV and V are recovered unchanged (96%) after being heated with a 1.5 M excess of KF(tech) in refluxing acetonitrile for 22.5 h. The silocin mixtures are readily reduced with $LiAlH_4$ to the corresponding silanes VI and VII (eq 6).

The ^1H NMR spectra of II and III show the characteristic FSiMe doublet between 0.4 and 0.6 ppm (J(HCSiF)



VI



(6)

VII

= 7.2 Hz) also reported for other heterocycles produced from ring expansion. The $SiCH_2$Arom absorption appears as a broad singlet in II and as an apparent doublet in III both of which are easily observed in mixtures which contain II and III. In the case of the reduced silocins VI and VII, the $SiCH_2$Arom absorption appears in the NMR spectra of both as an AB quartet split by SiH and in addition an SiH sextet is observed at about 4.5–4.8 ppm. Neither the ^1H nor ^{13}C NMR data could be used to uniquely define the structure of the major (or minor) silocin isomer generated in the ring expansion reaction. However, the distinction between these two isomers could be made from the mass spectral data, as illustrated in Scheme I. The mass spectrum of each silocin is characterized by elimination of O=SiMeH and hydrocarbon as well as hydrogen rearrangement followed by hydrocarbon loss. The ions generated in these processes clearly distinguish between VI and VII. For comparison, the data for the cleavage-derived ethers, IV and V, are also included.

These experiments demonstrate that eight-membered rings may be generated by anion-induced rearrangement of halomethyl-substituted silepins although not as smoothly nor in as high yields as has been demonstrated for six- to seven-membered ring conversions. Although both Ia and Ib may react completely with the fluoride ion, reactions other than silocin formation occur. The products of these alternate pathways were not analyzed but are probably oligomers since high-boiling, glassy residues are obtained after removal of the volatiles. Benzyl phenyl ether, which would be obtained from cleavage of Ia (or Ib), was not observed when starting materials were carefully purified. The highest yields of the eight-membered ring product are obtained from the iodomethyl precursor and when homogeneous conditions are employed for the rearrangement. The preparation of Ib requires an additional step. However, the combination of Ia/KF/KI actually generates both II and III, but III is consumed when additional KF is added at the end of the reflux period to complete the conversion of Ia. The conditions for maximum conversion of Ia to II and III with KF/KI were not determined.

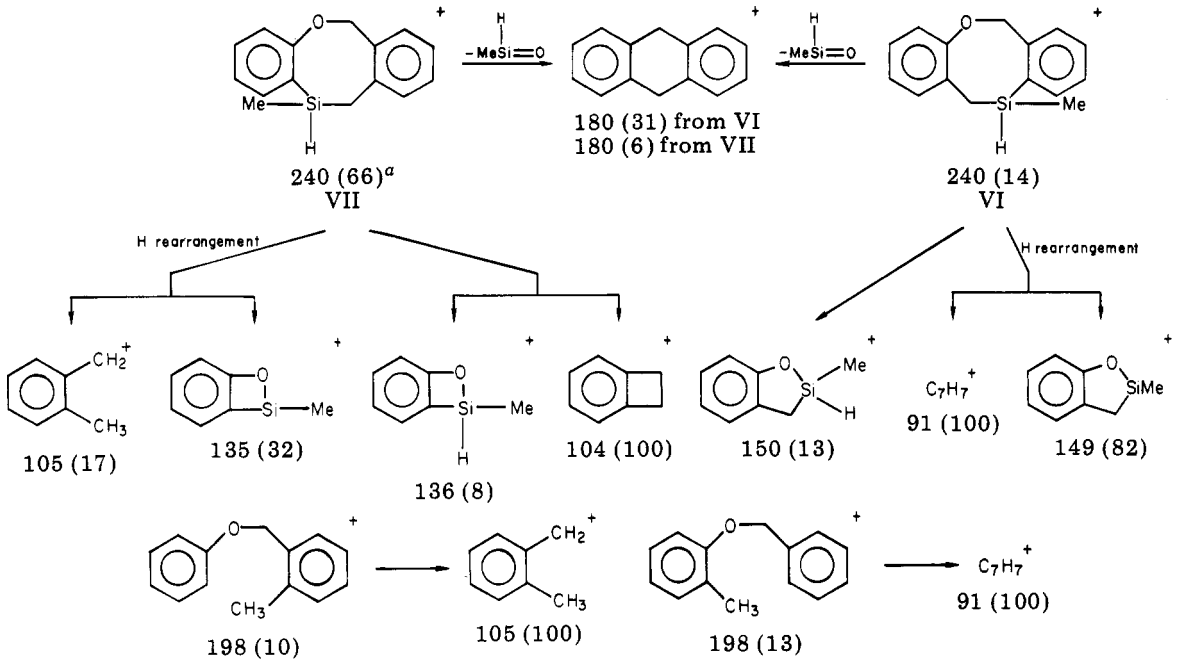
Experimental Section

General Data. All reactions which involved organolithium reagents, chlorosilanes, and Grignard reagents were carried out under an atmosphere of dry nitrogen in flame-dried glassware.

The organic halide *o*-$BrC_6H_4OCH_2C_6H_4Br$-*o* was prepared according to the literature method from *o*-$BrC_6H_4CH_2Br$ and *o*-BrC_6H_4OH.[6] The commercial reagents *o*-BrC_6H_4OH, *o*-$CH_3C_6H_4OH$, C_6H_5OH, $C_6H_5CH_2Br$, $MeSi(CH_2Cl)Cl_2$, *n*-BuLi, KF(tech), $Bu_4N^+F^-$/THF, KI, and $LiAlH_4$ were used as supplied. The technical KF samples employed in this study contained 15% by weight of water (determined by heating to constant weight

(6) Auwers, *Justus Liebigs Ann. Chem.* **1870**, *357*, 90.

Scheme I



[a] *m/e* (%).

at 110 °C). The *o*-$BrC_6H_4CH_2Br$ was prepared by bromination (Br_2) of *o*-$BrC_6H_4CH_3$.[7]

Tetrahydrofuran was dried by treatment with *n*-BuLi (*o*-phenanthroline indicator) followed by distillation,[8] and acetonitrile was dried over molecular sieves a minimum of 2 days prior to use.

Proton NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrophotometer (internal Me_4Si as reference (ppm) unless otherwise specified). Mass spectral data were collected at 70 eV on an AEI MS-1201 B or an HP 5985A GC/MS mass spectrometer. The Kugelrohr distillation method was employed in all vacuum distillations.

Analyses were performed by Galbraith Laboratories, Inc., and by Miles Laboratories.

11-(Chloromethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*]-[1,4]oxasilepin, Ia. The oxepin, Ia, was prepared by the published procedure[1] from *o*-bromobenzyl *o*-bromophenyl ether (21 g, 0.061 mol), *n*-BuLi (7.7 g, 0.12 mol), and methyl(chloromethyl)dichlorosilane (10 g, 0.061 mol). After aqueous workup and removal of the solvent from the organic layer, Kugelrohr distillation of the resultant oil provided two fractions, 6.8 g boiling at 140–155 °C (0.05mmHg) and 1.7 g boiling at 155–175 °C (0.05mmHg) both of which contained Ia. The lower boiling fraction contains a benzyl phenyl ether impurity which is partially removed by redistillation or chromatography over silica gel.

Chromatographic purification of 1.5–2.0 g portions of each fraction (40 g of silica gel, 2:3 and 1:1 benzene–hexanes mixtures as eluant) gave Ia (5.8 g, 35%): ^1H NMR ($CDCl_3$) δ 7.8–6.7 (m, Arom), 5.4–4.9 (q, OCH_2), 3.4 (s, CH_2Cl), 0.85 (s, $SiCH_3$); *m/e* mass spectrum, (relative intensity) 274 (1.1), 225 (100), 197 (10), 165 (33), 147 (12). Presence of an impurity (5–8%) is indicated by an OCH_2 singlet at 5.1 ppm and enhanced aromatic absorption.

An analytical sample of Ia, obtained as a colorless oil, was prepared by column chromatography of purified samples of Ia (silica gel, 1:4 chloroform–*n*-hexanes mixture as eluant). (Anal. Calcd for $C_{15}H_{15}OSiCl$: C, 65.57; H, 5.46. Found: C, 65.63; H, 5.52.)

11-(Iodomethyl)-11-methyl-5,11-dihydrodibenzo[*b*,*e*]-[1,4]oxasilepin, Ib. A 2.9-g sample of crude, distilled Ia (80% Ia, 2.3 g, 8.5 mmol) was heated at reflux with KI (2.73 g, 16 mmol) in CH_3CN (50 mL) for 7 h. After removal of the solvent, the residue was treated with ether–water and the oil obtained from the ether layer was purified by column chromatography (50 g of silica gel, 3:2 and 1:1 hexanes–benzene mixtures as eluant) to give Ib (2.71 g, 87%). The eluted fractions consistently contained about 10% by weight of an impurity which could be removed by heating samples up to 130 °C (0.05mmHg) to eliminate the volatiles: ^1H NMR ($CDCl_3$) δ 7.7–6.9 (m, 8.3, arom), 5.5–4.9 (q, 1.7, OCH_2), 2.6 (s, 2.0, CH_2I), 0.73 (s, 3.0, $SiCH_3$). A sample was further purified by column chromatography (silica gel, 1:4 chloroform–*n*-hexane mixture as eluant) but Ib, a colorless oil, still contained minor impurities. (Anal. Calcd for $C_{15}H_{15}OSiI$: C, 49.18; H, 4.10. Found: C, 50.02; H, 4.60.) No further effort was made to obtain an analytical sample.

Benzyl *o*-Tolyl Ether, IV. To a solution of sodium ethoxide prepared from sodium (2.3 g, 0.10 mol) and ethanol (50 mL) was added *o*-cresol (10.8 g, 0.100 mol). The mixture was stirred for 10 min and α-bromotoluene (17.1 g, 0.100 mol) added. After 20 min at room temperature, the solution was heated at reflux until the solution tested neutral. After extraction with ether and removal of the solvent, Kugelrohr distillation of the resultant oil gave 8.7 g (44%) of IV as a colorless oil: bp 110–115 °C (0.1mmHg) [lit. 110 °C (0.01mmHg)];[5] ^1H NMR ($CDCl_3$) δ 7.4–6.5 (m, 9.3, arom), 4.9 (s, 1.8, OCH_2), 2.2 (s, 2.9, CH_3); mass spectrum, *m/e* (relative intensity) 198 (14), 105 (13), 91 (100).

Phenyl *o*-Xylyl Ether, V. To a solution of sodium ethoxide prepared from sodium (3.2 g, 0.14 mol) and ethanol (100 mL) was added phenol (14 g, 0.15 mol). After the mixture had been stirred for 10 min, crude *o*-methylbenzyl bromide [prepared from *o*-xylene (16 g, 0.15 mol) and *N*-bromosuccinimide (2.7 g, 0.15 mol)] was added, whereupon NaBr begins to precipitate. The reaction mixture was heated at reflux for 1 h, the solvent removed, and the residue extracted with ether–water. The residue obtained from evaporation of the ether layer was distilled to give 18 g (61%) of V, bp 100–120 °C (0.05mmHg), which slowly solidified. Recrystallization of the solid from ethanol gave white crystals: mp 50–51 °C; ^1H NMR ($CDCl_3$) δ 7.5–6.7 (m, 9.3, arom), 4.9 (s, 1.8, OCH_2), 2.3 (s, 2.9, CH_3); mass spectrum, *m/e* (relative intensity) 198 (10), 105 (100), 91 (19), 77 (10). (Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.84; H, 7.13.)

Reaction of Ia and Ib with Fluoride Sources. A sample of (halomethyl)silepin and the metal salt were heated at reflux in acetonitrile until an aliquot showed that no or only minor amounts of I remained. The solvent was removed, hexanes were added to the residue, and insoluble material was removed by filtration. The oil obtained on concentration of the hexanes solution was distilled and all material with a boiling point up to 130–135 °C (0.05mmHg) was collected. Unreacted I was generally recovered from fractions with a boiling point of 135–150 °C

(7) Letsinger, R. I.; Skoog, I. H. *J. Am. Chem. Soc.* **1955**, *77*, 5176.
(8) Purdum, W. R.; Bartling, G. J. *J. Chem. Educ.* **1975**, *52*, 120.

Table I. Reaction of 5-(Halomethyl)-5-methyl-5,11-dihydrodibenzo[*b*,*e*][1,4]oxasilepin, I, with Fluoride Sources

I, g	F^- sources	F^-/I	*T*, °C (*t*, h)	distilled product,[a] g	product,[b] g: silocins	product,[b] g: cleavage ethers	recovered I,[c] g	sum II, III, IV, and IV,[a] %
Ia								
2.91[e]	KF/crown[f]	1.6	80 (24)	1.1	trace	0.72 (IV + V)[g,h]		30–35
3.0[e]	KF/crown	1.0	80 (9)	0.80	0.18 (II)	0.31 (IV + V)	0.36	26
2.89[i]	$Bu_4N^+F^-$	1.4[j]	20 (1)	0.88[k]	(II)			
2.93[i]	$Bu_4N^+F^-$	1.1	20 (0.8)	1.21	0.52 (II)[l,m]	0.11 (IV + V)[m]	0.30	29
1.38[i]	KF/KI[n]	1.0[o]	80 (20)	*p*	0.39 (II)	0.04 (V)		34
Ib								
0.93[e]	KF	1.0	80 (11)	0.37	} 0.49 (II + III)[q]	0.06 (IV + V)		29
2.00[e]	KF	2.0	80 (9)	0.67				
2.39[r]	KF	1.1	80 (10)	1.10	0.24 (III)[h] 0.54 (II)[h]		0.13	48
3.21[i]	$Bu_4N^+F^-$	1.07	20 (1)	1.32	0.38 (III)[l,h] 0.72 (II)[l,h]		0.40	67[s]
0.18[i]	AgF	2.0	20 (16)		(II) (43%)[t]		(16%)[t]	

[a] bp <135 °C (0.1 mm). [b] Distilled samples eluted over silica gel unless otherwise indicated. [c] Isolated from fractions with bp >135 °C (0.1 mm). [d] Corrected for any recovered starting material. [e] Distilled sample (estimated, 85% Ia). [f] No reaction in the absence of crown ether. [g] Contains unidentified benzyl phenyl ether (estimated 0.2 g). Ratio of V/IV = 2.5. [h] Isomer distribution estimated from ^1H NMR spectra. [i] Samples purified by distillation followed by chromatography. [j] Added in three increments until Ia disappeared. [k] Only silocin II is observed in addition to cleavage products. [l] Distilled product reduced with $LiAlH_4$ before elution over silica gel. [m] Product distribution estimated from ^1H NMR spectra of eluted fractions. [n] KF/KI = 10. [o] Ratio increased to 1.1 after 15 h of reflux to complete conversion of Ia. [p] Product eluted directly over silica gel. [q] Contains Ib. [r] Sample purified by elution over silica gel. [s] Includes partial silocin cleavage product *o*-$(CH_3SiH_2)C_6H_4OCH_2C_6H_4CH_3$-*o* or isomer. [t] Estimated from NMR data.

(0.05mmHg). The lower boiling fraction was chromatographed over silica gel.

Reactions with *n*-$Bu_4N^+F^-$ were carried out in THF for 30–60 min. A precipitate of *n*-$Bu_4N^+I^-$ formed in reactions of Ib. After the reaction period, the solvent was removed and the residue treated with ether–water. The ether was removed from the organic layer, and the oil was distilled and then chromatographed as described for reactions with metal salts.

The results are summarized in Table I.

11-Methyl-11-fluoro-11,12-dihydro-6*H*-dibenzo[*b*,*f*][1,5]-oxasilocin, II, and 12-Methyl-12-fluoro-11,12-dihydro-6*H*-dibenzo[*b*,*f*][1,4]oxasilocin, III. A 2.39-g sample of (iodomethyl)silepin, Ib (purified by column chromatography and was 90% Ib, 5.9 mmol), 0.49 g of KF(tech) (85% KF, 7.2 mmol), and acetonitrile (50 mL) were heated at reflux for 10 h. The solvent was removed, hexanes were added to the residue, and insoluble material (0.69 g of a mixture of KF and KI) was removed by filtration. Kugelrohr distillation of the oil recovered from the hexanes gave a mixture of the silocins (1.10 g), bp 105–130 °C (0.05mmHg), and starting material (0.13 g), bp 130–145 °C (0.05mmHg). Column chromatography of the distilled oil (40 g of silica gel, eluant as indicated) gave a total of 0.83 g (58%) of silocins II and III as colorless oils.

The fraction which eluted with 1:1 benzene–hexanes contained 0.42 g of II contaminated with traces of a benzyl phenyl ether impurity: ^1H NMR ($CDCl_3$) δ 8.1–6.7 (m, arom), 5.6–5.0 (q, OCH_2), 2.3–2.1 (br m, $SiCH_2$), 0.58–0.47 (d, $FSiCH_3$); mass spectrum, *m*/*e* 258 (M^+). An attempt to prepare an analytical sample of II by further column chromatography over silica gel was not successful.

The fraction which eluted with 3:2 benzene–hexanes contained 0.27 g of a mixture of II and III. The fraction which eluted with 7:3 benzene–hexanes contained 0.14 g of silocin III: ^1H NMR ($CDCl_3$) δ 7.8–6.5 (m, 8.2, arom), 5.3–4.8 (q, 2.1, CH_2), 2.6–2.5 (apparent d, 1.7, $SiCH_2$), 0.53–0.40 (d, 3.0, $FSiCH_3$); mass spectrum, *m*/*e* 258 (M^+). (Anal. Calcd for $C_{15}H_{15}FOSi$: C, 69.77; H, 5.81. Found: C, 69.28; H, 5.88.) An attempt to further purify III resulted in decomposition of the sample.

11-Methyl-11,12-dihydro-6*H*-dibenzo[*b*,*f*][1,5]oxasilocin, VI, and 12-Methyl-11,12-dihydro-6*H*-dibenzo[*b*,*f*][1,4]oxasilocin, VII. To a sample of Ib (3.21 g, which had been purifed by removing volatiles with a boiling point below 130 °C (0.05mmHg) followed by column chromatography of the residue over silica gel, 8.8 mmol) dissolved in tetrahydrofuran (50 mL) was added dropwise a solution of $Bu_4N^+F^-$ (9.4 mL, 1.0 M). The solution was stirred at room temperature for 1 h during which time a precipitate formed. The solvent was evaporated and the residue extracted with water–ether followed by filtration to remove *n*-$Bu_4N^+I^-$ (2.73 g, 85%). Kugelrohr distillation of the residue obtained from the ether layer gave a mixture of II and III [1.32 g, 72% based on recovered starting material, bp 108–128 °C (0.1mmHg)] and starting material [0.4 g, bp 135–150 °C (0.1mmHg)].

The mixture of silocins was treated with $LiAlH_4$ (0.95 g, 25 mmol) in refluxing ether for 1 h. An oil was obtained from the organic layer after hydrolytic workup. Column chromatography of the oil (50 g of silica gel, eluant as indicated) gave a total of 1.10 g (62%) of silocins IV and V as colorless oils.

The fraction which eluted with 2:3 benzene–hexanes contained 0.58 g of VI: ^1H NMR ($CDCl_3$) δ 7.6–6.7 (m, 8.3, arom), 5.3 (s, 1.8, OCH_2), 4.9–4.6 (m, 1.1, SiH), 2.6–1.9 (AB portion of an ABX multiplet centered at 2.25, 1.8, $SiCH_2$), 0.48–0.47 (d, 2.9, $HSiCH_3$); mass spectrum, *m*/*e* (relative intensity) 240 (14), 239 (11), 225 (53), 180 (31), 179 (70), 178 (41), 163 (35), 166 (13), 150 (13), 149 (83), 135 (11), 121 (13), 91 (100). The silocin VI was further purified by additional column chromatography over silica gel. (Anal. Calcd for $C_{15}H_{16}OSi$: C, 75.00; H, 6.67. Found: C, 75.05; H, 6.82.)

The next fraction which eluted with 1:1 benzene–hexanes contained 0.42 g of a mixture of both VI and VII as well as a trace of 5,5-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin. The fraction which eluted with 3:2 benzene–hexanes contained 0.20 g of VII: ^1H NMR ($CDCl_3$) δ 7.4–6.6 (m, 8.1, arom), 5.1 (s, 2.0, OCH_2), 4.7–4.3 (sextet, 0.9, SiH), 2.8–2.2 (AB portion of an ABX multiplet centered at 2.5, 1.9, $SiCH_2$), 0.38–0.32 (d, 3.0, $SiCH_3$); mass spectrum, *m*/*e* (relative intensity) 240 (66), 180 (6), 166 (3), 165 (10), 136 (8), 135 (32), 121 (20), 105 (17), 104 (100). The silocin VII was further purified by additional column chromatography over silica gel. (Anal. Calcd for $C_{15}H_{16}OSi$: C, 75.00; H, 6.67. Found: C, 74.25; H, 6.78.) Further efforts to obtain an anlytical sample of VII resulted in decomposition.

The earliest fraction which eluted with 1:4 benzene–hexanes contained 0.09 g of an oil which was tentatively identified as *o*-$(CH_3SiH_2)C_6H_4OCH_2C_6H_4CH_3$-*o* or its isomer: ^1H NMR ($CDCl_3$) δ (in part) 4.5–4.3 (q, SiH), 0.30–0.16 (t, $SiCH_3$).

Reaction of II with KF/18-Crown-6. A solution of II (0.40 g, 1.5 mmol) and 18-crown-6 (0.05 g) in acetonitrile (25 mL) was heated at reflux with KF(tech) (85% KF, 0.15 g, 2.2 mmol) for 18 h. The solvent was removed and the residue extracted with ether–water. The ether layer was dried over Na_2SO_4, and upon removal of ether, IV (0.28 g, 91%) was obtained which was identical with an authentic sample.

Reaction of III with KF(tech). A solution of III (0.08 g, 0.3 mmol) in acetonitrile (5 mL) was heated at reflux with KF(tech) (85% KF, 0.03 g, 0.4 mmol) for 18 h. After removal of the solvent

an NMR spectrum of the residue showed only the presence of V.

Reaction of IV with KF(tech). A solution of IV (1.41 g, 7.12 mmol) in acetonitrile was heated at reflux with KF(tech) (85% KF, 0.64 g, 9.4 mmol) for 22.5 h. After removal of the solvent, the residue was extracted with ether–water and the ether layer dried over Na_2SO_4. Removal of the ether resulted in the recovery of IV (1.36 g, 96%).

Reaction of V with KF(tech). A solution of V (1.82 g, 9.2 mmol) in acetonitrile (50 mL) was heated with KF(tech) (85% KF, 0.83 g, 12 mmol) at reflux for 22.5 h. After workup, V (1.79 g, 98%) was recovered.

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Registry No. Ia, 71445-87-9; Ib, 80532-94-1; II, 80532-95-2; III, 80532-96-3; IV, 19578-70-2; V, 57076-47-8; VI, 80532-97-4; VII, 80532-98-5; *o*-bromobenzyl *o*-bromophenyl ether, 5310-54-3; *o*-cresol, 95-48-7; α-bromotoluene, 100-39-0; phenol, 108-95-2; *o*-methylbenzyl bromide, 89-92-9.

Reaction of Secondary and Tertiary Alkyllithium Reagents with Vinyl Di- and Trisiloxanes. Synthesis of α-Silyl Silanols

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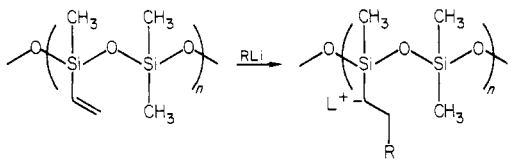
Secondary and tertiary alkyllithiuim reagents add to the carbon–carbon double bond of vinyl di- and trisiloxanes at low temperature (−78 °C) to yield α-lithioalkyl di- and trisiloxanes. If these are quenched with moist THF at low temperature alkyl di- and trisiloxanes are formed. However, if such α-lithioalkyl di- and trisiloxanes are warmed to 0 °C prior to quenching, α-silyl silanols are found. These products result from a 1,3 rearrangement of a silyl group from oxygen to the carbanion center. This converts the carbanion into an alkoxide anion. The scope and generality of these reactions have been explored.

We have been interested recently in developing methods to modify siloxane polymers. Despite previous reports that organolithium reagents easily cleave hexaorganodisiloxanes to yield tetraorganosilanes and lithium triorganosilanoates,[1] the possible addition of alkyllithium reagents to the

$$Ph_3SiOSiPh_3 + PhLi \rightarrow Ph_4Si + Ph_3SiO^-Li^+ \quad (1)$$

carbon–carbon double bond of vinyl methyl siloxanes seemed worthy of examination.



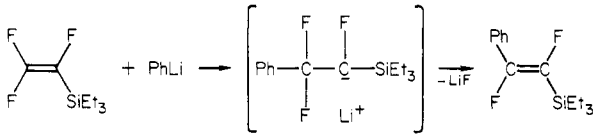
(2)

The addition of Grignard and organolithium reagents to vinylsilanes to yield α-silyl organometallics has been known for almost 30 years.[2–5]

$$Ph_3Si{-}CH{=}CH_2 + PhLi \rightarrow Ph_3Si{-}{}^-CH{-}CH_2{-}Ph \quad Li^+ \quad (3)$$

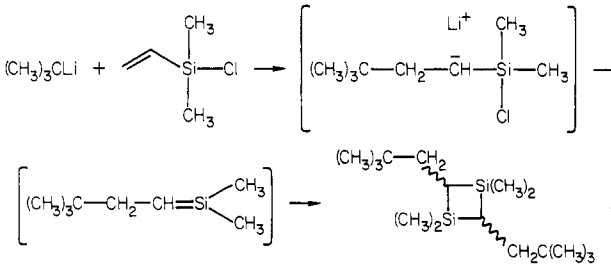
Such α-silyl organometallics have proved useful for the preparation of substituted alkenes via the Peterson olefination reaction.[6,7]

However, addition of organolithium reagents to (β-halovinyl)silanes or to vinylchlorosilanes yield α-silyl organometallics which may undergo elimination of the elements of lithium halide. This may result in the formation of a carbon–carbon double bond or reactive silicon–carbon doubly bonded intermediate. For example, addition of organolithium reagents to perfluorovinyltriethylsilane results in an α-silyl organolithium intermediate which undergoes loss of lithium fluoride to yield (β-organo-α,β-difluorovinyl)triethylsilanes (eq 4),[8,9] while addition of



(4)

tert-butyllithium to vinyldimethylchlorosilane gives substituted 1,3-disilacyclobutanes.[10–12] The formation of these compounds have been interpreted in terms of addition of the organolithium reagent to the vinylchlorosilane to yield an α-silyl organolithium reagents which undergoes loss of lithium chloride to yield a reactive intermediate possessing a silicon–carbon double bond. These dimerize in a head-to-tail manner to yield the products observed (eq 5).



(5)

(1) H. Gilman, H. N. Bendict, and H. Hartzfeld, *J. Org. Chem.* **19**, 419 (1954).
(2) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952).
(3) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).
(4) J. F. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965).
(5) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970).
(6) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).
(7) For a review see: D. J. Peterson, *J. Organomet. Chem. Libr.*, **7**, 295 (1972).
(8) D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Lett.*, 20 (1960).
(9) D. Seyferth and T. Wada, *Inorg. Chem.* **1**, 78 (1962).
(10) P. R. Jones and T. F. O. Lin, *J. Am. Chem. Soc.*, **99**, 2013 (1977).
(11) P. R. Jones and T. F. O. Lin, *J. Am. Chem. Soc.*, **99**, 8447 (1977).
(12) P. R. Jones, T. F. O. Lin, and R. A. Pierce, *J. Am. Chem. Soc.*, **102**, 4970 (1980).

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