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Organosilicon compounds with functional groups proximate to silicon

XVII *. Synthetic and mechanistic aspects of the lithiation of α,β-epoxyalkylsilanes and related α-heterosubstituted epoxides **

John J. Eisch and James E. Galle

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901 (U.S.A.)

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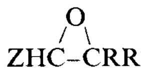
Abstract

A series of α-heterosubstituted epoxides,  $\mathrm{ZH\overset{\overset{O}{/\ \backslash}}{C-C}RR'}$, has been found to undergo lithiation in the temperature range of -75 to $-115\,^\circ\mathrm{C}$ at the C–H bond of the epoxide. The substituent Z could be Me_3Si, Ph_3Si, n-Bu_3Sn, Ph_3Sn, $PhSO_2$, $(OEt)_2PO$ and Ph; the groups R and R′ were H, Ph and n-C_6H_{13}; and the lithiating reagents were n-butyllithium, t-butyllithium and lithium diisopropylamide in donor media of THF or TMEDA. The lithiation occurs with retention of configuration and the resulting lithio-epoxide is unstable above 0 °C, decomposing in a carbenoid manner. The lithiation is facile except for compounds where Z and R (an alkyl or aryl) are *cis*-oriented; where $Z = R_3Sn$, lithiation occurs by tin–lithium, rather than hydrogen–lithium, exchange. The lithio-epoxides thereby generated can be quenched with various reagents to yield epoxides where the epoxide H has been replaced by D, Me_3Sn, R, RCO and COOH. The utility of this procedure in organic synthesis is emphasized. Finally, the possible explanations for the acidity of such α-heterosubstituted epoxides and for the relative stability of the derived lithio-epoxides are considered and assessed.

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* For previous part, refer to ref. 5.

** Dedicated to Professor Colin Eaborn for his masterly application of physical organic chemistry to elucidating the chemistry of organosilicon compounds.

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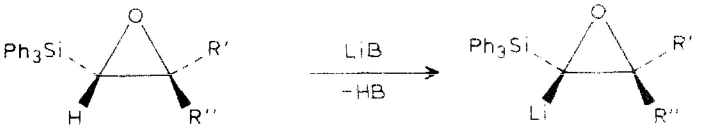
Introduction

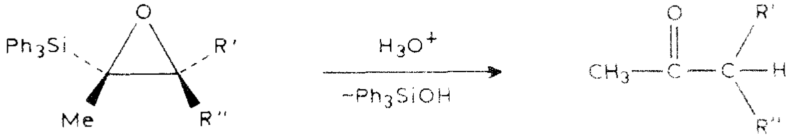
In the quarter century since the publication of Colin Eaborn's pioneering monograph, Organosilicon Compounds [1], many chemists throughout the world have initiated research on the chemistry of organosilanes. Whether such studies involved the mechanisms of organosilicon reactions [2] or the application of functionally substituted organosilanes to organic synthesis [3], Eaborn's perceptive survey has been the chemist's vade mecum. In our laboratory we have been intrigued by the unusual acidifying effect that a silicon exerts upon an adjacent C–H bond, in general [4,5], and a proximate epoxide in particular [6,7] (eq. 1).



(1)

(I) (II)

We were interested not only in the electronic origin and mechanistic aspects of this reaction, but also in the scope and utility of such α-lithioepoxyalkanes in organic synthesis. To this end, a variety of epoxides of known stereochemistry ($R' \neq R''$) and having other heteroatoms in place of Si (with Sn, RO_2S, $(EtO)_2PO$ or R) were treated with different lithiating agents LiB (B = n-Bu, t-Bu, Ph and i-Pr_2N). The resulting α,β-epoxyalkyllithium reagents were then converted into a gamut of silyl, stannyl, alkyl, acyl and carboxyl derivatives, in order to learn whether II and its derivatives could serve as epoxide or carbonyl synthons in the construction of carbon skeletons. It should be noted that the carbon–lithium bond of II makes the epoxide carbon nucleophilic toward the electrophilic carbon in alkyl halides or carbonyl derivatives. Furthermore, once derivatized, α-silylepoxides can be hydrolyzed to yield silicon-free carbonyl derivatives [8] (eq. 2).



(2)

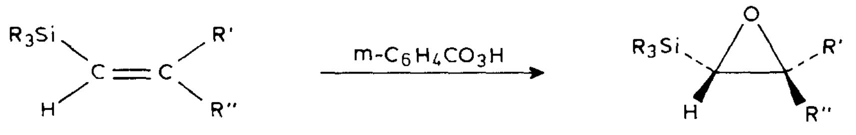
(III) (IV)

Results

Lithiation of α-heterosubstituted epoxides

α,β-Epoxyalkylsilanes. The epoxides Va–XIa were prepared from the corresponding olefins by epoxidation with *m*-chloroperbenzoic acid: trimethyl(vinyl)silane (V), triphenyl(vinyl)silane (VI), *cis*-1,2-deuterioethenyl(triphenyl)silane (VII), trimethyl(*cis*-1-octenyl)silane (VIII), *trans*-1-octenyl(triphenyl)silane (IX), trimethyl(*cis*-β-styryl)silane (X) and trimethyl(*trans*-β-styryl)silane (XI) (eq. 3).

These epoxides could be lithiated with varying ease, either with n-butyllithium in THF at −78°C or with the t-butyllithium-TMEDA complex in hexane at −95°C (Table 1). Successful lithiation and its molecular site could be ascertained by two methods: quenching the lithium derivative (Vb–XIb) with D_2O and observing which



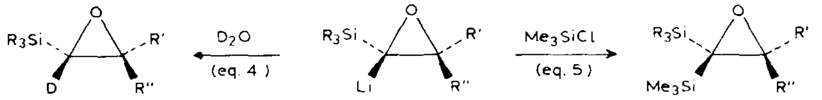
(3)

(V–XI) (Va–XIa)

(V : R = Me ; R', R" = H ;
VI : R = Ph ; R', R" = H ;
VII : R = Ph ; R' = H ; R" and H = D;
VIII : R = Me ; R' = C_6H_{13} ; R" = H)

(IX : R = Ph ; R' = H ; R" = C_6H_{13} ;
X : R = Me ; R' = Ph ; R" = H ;
XI : R = Me ; R' = H ; R" = Ph)

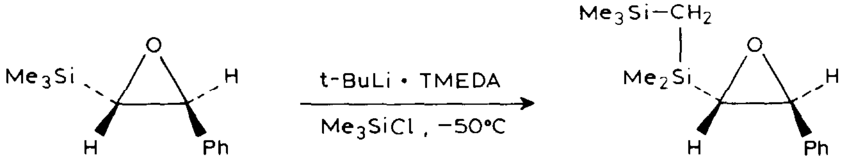
proton signal diminished in the ^1H NMR spectrum of recovered epoxide V–XI (eq. 4); or trapping the lithium intermediate by Me_3SiCl present during the lithiation (eq. 5).



(4,5)

(Vc–XIc) (Vb–XIb) (Vd–XId)

Such lithiations were essentially quantitative and took place at the C–H bond of the epoxide α to the silicon, except for the *cis*-epoxide Xa and the two *trans*-substituted epoxides, IXa and XIa. *cis*-Epoxide Xa was smoothly lithiated principally at the C–H α to the phenyl. This shows that the phenyl is more acidifying than the Me_3Si group. The latter two underwent lithiation much less readily (no reaction with n-BuLi in THF at −78 °C), probably due to steric hindrance in the approach of RLi to the C–H bond. In fact, XIa did not react at the C–H bond of its epoxide, but rather at a C–H bond of its Me_3Si group (eq. 6) *.



(6)

(XIa) (XII)

That these lithiations occur with retention of configuration and maintain their stereochemical integrity at low temperatures was demonstrated by the lithiation of *cis*-dideuterioepoxyethylsilane VII (eq. 7).

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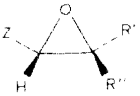
* Such lithiation of a trimethylsilyl group has been encountered in the reaction of $(Me_3Si)_2CPhCH_2Ph$ with alkyllithium reagents in TMEDA: ref. 9.

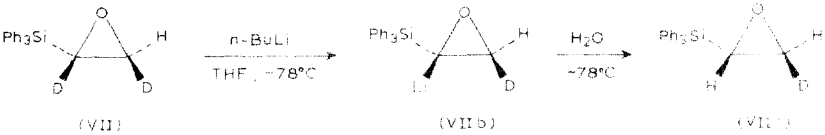
Table 1

The lithiation of heterosubstituted epoxides



Epoxide	Base, RLi	Temperature [a] (°C)	Quenching agent	Yield (%)
Va: Z = Me_3Si; R',R'' = H	t-BuLi, TMEDA	−95	Me_3SiCl [b]	75
VIa: Z = Ph_3Si; R',R'' = H	t-BuLi, TMEDA	−95	$PhCONEt_2$ [c]	65
	n-BuLi, THF	−78	D_2O	~100
	n-BuLi, TMEDA	−78	D_2O	~100
	n-BuLi, THF	−78	MeI [d]	91
	n-BuLi, THF	−78	$\mathrm{PhCO}\overline{\mathrm{NCH_2CH_2}}$	78
	n-BuLi, THF	−78	Me_3SnCl [b]	55
VIIIa: Z = Me_3Si; R' = C_6H_{13}; R'' = H	t-BuLi, TMEDA	−78	D_2O	79
	t-BuLi, TMEDA	−90	MeI [d]	81
IXa: Z = Ph_3Si; R' = H; R'' = C_6H_{13}	n-BuLi; TMEDA	−78	D_2O	~50
Xa: Z = Me_3Si; R' = Ph; R'' = H	t-BuLi, TMEDA	−78	Me_3SiCl [b,e]	83
XIa: Z = Me_3Si; R' = H; R'' = Ph	t-BuLi, TMEDA	−78	Me_3SiCl [b,f]	~50
XVIIIa: Z = Ph_3Sn; R',R'' = H	n-BuLi, THF	−85	H_2O [g]	~100
XIXa: Z = n-Bu_3Sn; R' = H; R'' = C_6H_{13}	t-BuLi, THF	−95	H_2O [h]	~100
XXIIa: Z = $(OEt)_2PO$; R',R'' = H	LiN-i-Pr_2	−115	Me_3SiCl [b]	91
	LiN-i-Pr_2	−115	MeI [d]	57
XXIIIa: Z = $PhSO_2$; R' = H; R'' = Ph	n-BuLi, THF	−110	D_2O	69
	n-BuLi, THF	−110	MeI [d]	62
XXIVa: Z = $PhSO_2$; R' = H; R'' = C_6H_{13}	n-BuLi, THF	−100	D_2O	~100

[a] For temperatures below −100 °C, a Trapp solvent was used: 3/1/1 of THF/hexane/ether. [b] Epoxide formed had a Me_3Si or Me_3Sn group on epoxide. [c] Derivative had a benzoyl group on epoxide. [d] Methylated epoxide was formed. [e] Me_3Si group attached α to phenyl group. [f] Me_3Si group attached to Me_3Si group. [g] Tetra-*n*-butyltin was formed. [h] Tri-n-butyl (t-butyl)tin was formed.



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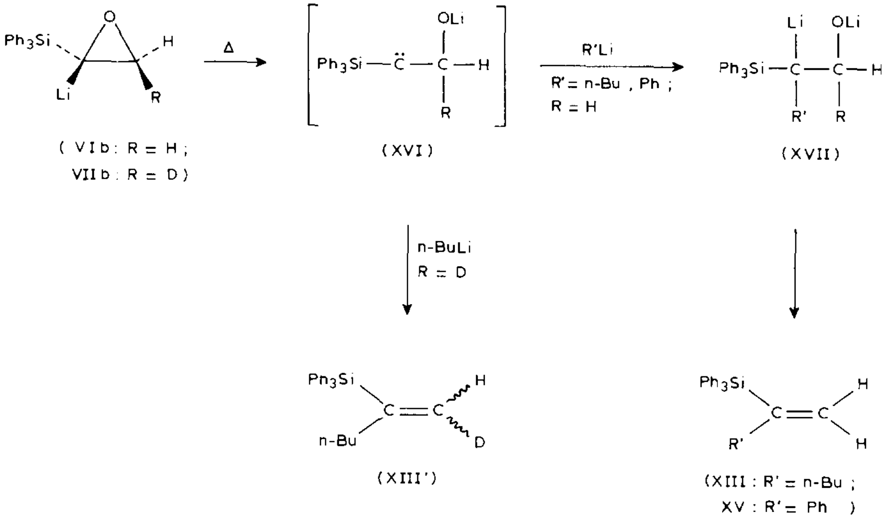

Scheme 1

The isolated VII′ was shown to be the *trans*-deuterio isomer by its ^{1}H NMR spectrum: the spectrum of VIIa (2.45 (d of d, 2-*cis* H, J_{gem} 5.5 Hz; J_{trans} 4.2 Hz); 2.85 (m, 1- and 2-*trans*) [11]) had changed in VII′ to signals at 2.45 (m of 4 Hz width) 1H and 2.85 (d, J_{trans} 4.2 Hz) 1H. However, the lithium reagent VIIb could decompose in another way than by isomerization, namely by α-elimination to yield a carbene (Scheme 1). In attempts to trap such carbene or carbenoid intermediates, VIIb was allowed to warm to 25°C in the presence of excess n-butyllithium. Hydrolytic workup yielded 73% of 1-hexen-2-yl(triphenyl)silane (XIII) and 15% of n-butyl(triphenyl)silane (XIV). Alternatively, when VIIb was formed with n-butyllithium and then an excess of phenyllithium was added, workup provided an 80% yield of triphenyl(1-phenyl-1-ethenyl)silane (XV). Finally, as a probe of stereochemistry, VIIb was permitted to react with an excess of n-butyllithium upon warming. The deuterated XIII′ was shown by ^{1}H NMR spectroscopy to be a 1/1 mixture of (*Z*)- and (*E*)-2-deuterio isomers. All these results are consistent with a mechanistic pathway in which the lithio intermediate VIb yields the carbenoid XVI by α-elimination and XVI then adds RLi nonstereoselectively, to form intermediates like XVII, which can readily eliminate lithium oxide *.

The presence of a donor solvent is essential for these lithiations. In the absence of a donor, the reaction ultimately takes a different course. Thus, n-butyllithium in hexane does not react with VI at −78°C; in refluxing hexane it converts VI into n-butyl(triphenyl)silane (XIV, 69% isolated yield, eq. 8). From the behavior of VI towards phenyllithium [1] and the reactions of epoxyalkyltins described below, this reaction clearly involves attack of the RLi at silicon and the displacement of CH_2CHOLi.

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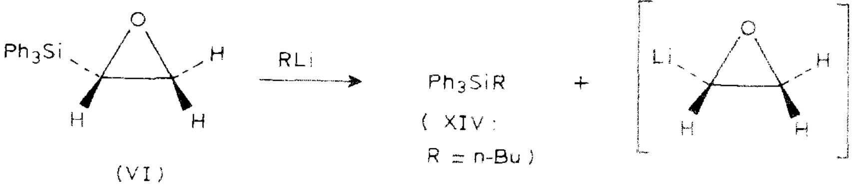
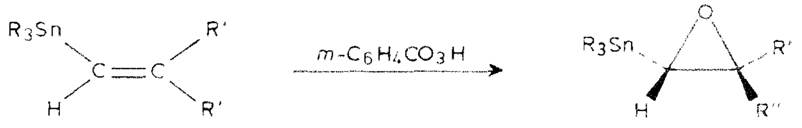
* The elimination of lithium oxide has been invoked in the reactions of ordinary epoxides with t-butyllithium [10].



(8)

α,β-Epoxyalkyltins. Two examples of these unusual organotin derivatives, namely epoxyethyl(triphenyl)tin (XVIIIa) and tri-n-butyl(*trans*-1,2-epoxy-1-octyl)tin (XIXa) could also be prepared from the vinyltins by using *m*-chloroperbenzoic acid under mild conditions (eq. 9).

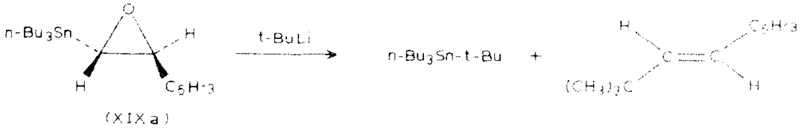


(9)

(XVIII : R = Ph; R', R'' = H;
XIX : R = n-Bu; R' = H; R'' = C_6H_{13}) (XVIIIa, XIXa)

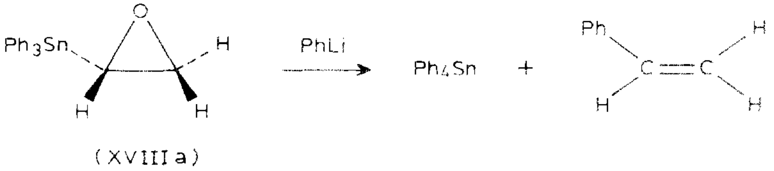
Even at 10–25 °C, some protodestannylation of the vinyltin was observed. Indeed, attempted epoxidation of tri-n-butyl(*cis*-β-styryl)tin (XX: R = C_4H_9; R' = Ph; R'' = H) yielded only styrene.

Treatment of XIXa with n-butyllithium in hexane at −85 °C led to no reaction. However, a similar reaction in THF quantitatively converted XIXa into tetra-n-butyltin. The nature of the reaction became clearer when XIXa was treated with an excess of t-butyllithium in a Trapp solvent (THF/Et_2O/pentane) at −95 °C. Not only was tri-n-butyl(t-butyl)tin isolated, but also *trans*-2,2-dimethyl-3-decene could be obtained (eq. 10).



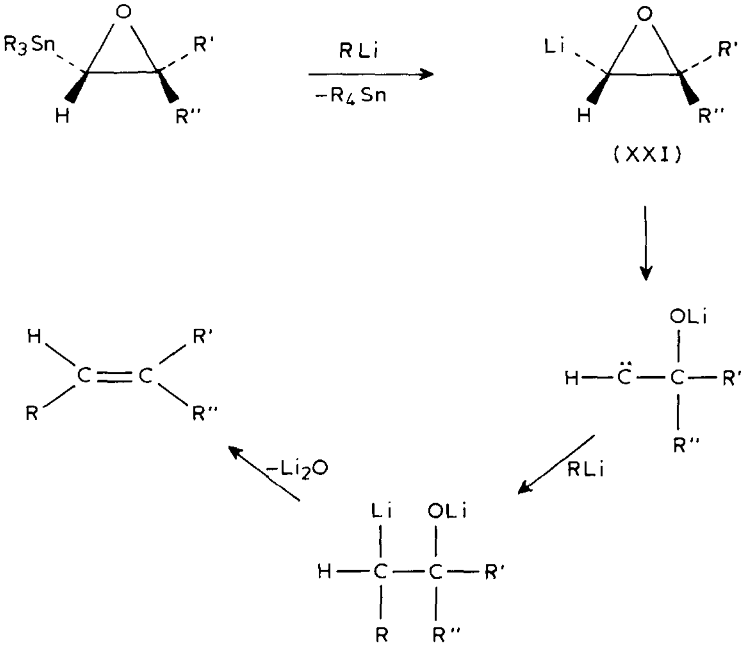
(10)

In an analogous manner, treatment of XVIIIa with phenyllithium in diethyl ether gave both tetraphenyltin and styrene (eq. 11).



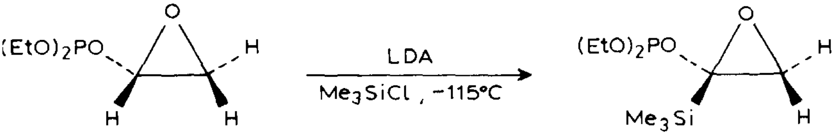
(11)

All the foregoing observations support the conclusion that such tin epoxides undergo rapid tin–lithium exchange (cf. eq. 8) and the resulting α-lithioepoxide (XXI) undergoes α-elimination and carbenoid reactions, analogous to those depicted in Scheme 1 (Scheme 2):



Scheme 2

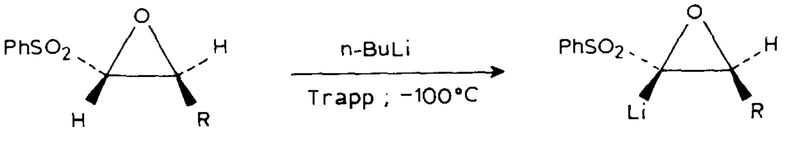
α,β-Epoxyalkylphosphonates. One example of such an ester, diethyl epoxyethylphosphonate (XXIIa) was examined carefully. It could be readily lithiated with lithium diisopropylamide (LDA) and the lithio intermediate (XXIIb) quantitatively captured by in-situ Me_3SiCl (eq. 12).



(12)

(XXIIa) (XXIId)

α,β-Epoxyalkyl sulfones. The two sulfones examined, *trans*-epoxystyryl phenyl sulfone (XXIIIa) and *trans*-1,2-epoxy-1-octyl phenyl sulfone (XXIVa) were extraordinarily easy to lithiate: short reaction times at −100 °C sufficed for complete conversion (eq. 13).



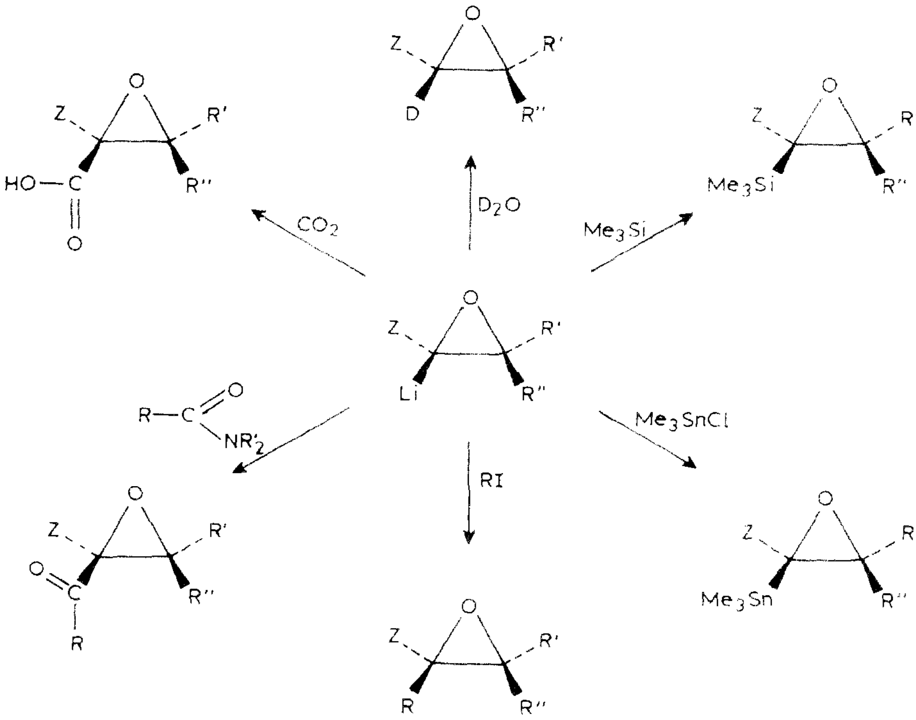
(13)

(XXIIIa : R = Ph ;
XXIVa : R = C_6H_{13})

(XXIIIb , XXIVb)

Derivatives from α-lithioepoxyalkanes

The lithiation products from these epoxides (Table 1, except those from tin epoxides) have proved most versatile in preparing a wide variety of organic



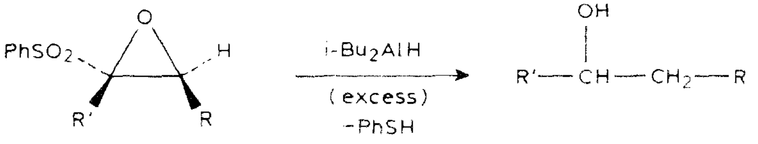
Scheme 3

derivatives. Although an exhaustive survey of possible substrates has not been completed, it is clear from our work that the following substituents can replace the lithium of Vb–XIb, XXIIb, XXIIIb and XXIVb in high yield: D, Me$_3$Si, Me$_3$Sn, R, R–CO and COOH (Scheme 3).

Derivatives of the resulting substituted epoxides

These syntheses from lithioepoxyalkanes, as depicted in Scheme 3, gain in utility from the accessibility of known reactions that can remove the heterosubstituent Z and convert the epoxide function to a carbonyl group (e.g., eq. 2), a vicinal glycol [12] or a hydroxyalkyl linkage [13]. Two such reactions were explored in this study: hydride reduction of these epoxides and fluorodisilylation of epoxyalkylsilanes without ring opening.

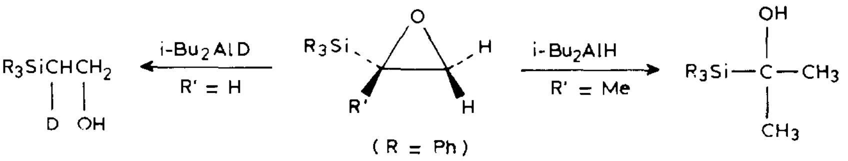
Diisobutylaluminum hydride in hexane reductively cleaves α,β-epoxyalkyl sulfones selectively at the C–O bond distal to the SO$_2$Ph group and removes the sulfur from the system (eq. 14).



(14)

(R' = H , D , Me ; R = Ph , 1-octyl)

Such reduction with α,β-epoxyalkylsilanes occur cleanly in one sense, but either

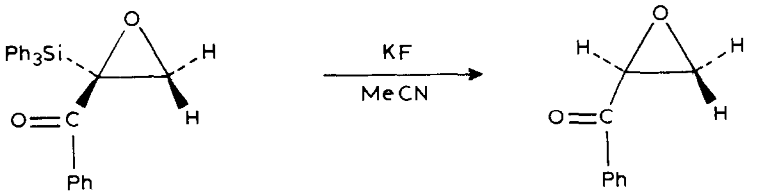


(15)

the C–O bond distal to or proximal to the silicon can be cleaved (eq. 15).

The deuteriation experiment demonstrates that the epoxide is cleaved without rearrangement to the aldehyde [13].

Finally, fluoride ion can desilylate such epoxides smoothly. However, in the case of α-acyl-α,β-epoxyalkylsilanes (XXV) the reaction is not stereoselective (eqs. 16 and 17) *.



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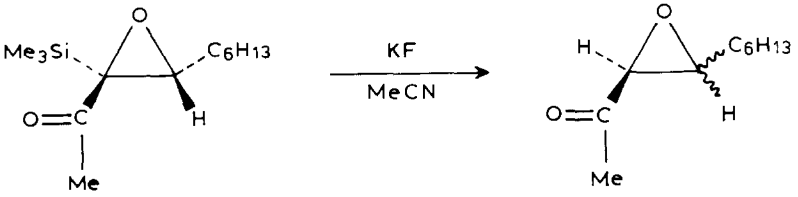

(17)

(XXV)

1/1 *cis/trans*

Discussion

The principal aspects of this study requiring further comment are the underlying reasons for the exceptional kinetic acidity of the α-protons in these epoxides and for the relative stability of the resulting lithium intermediates below −50 °C. Clearly, in both aspects the presence of the R_3Si, $PhSO_2$ and $(EtO)_2PO$ groups is decisive: ordinary epoxides, such as ethylene oxide, do not undergo lithiation with RLi but, instead, suffer ring cleavage to yield RCH_2CH_2OLi; also lithioepoxides, without these substituents, decompose at −85 °C to give carbenoids (cf. eqs. 10 and 11, and Scheme 2).

That the $PhSO_2$ and $(EtO)_2PO$ groups enhance the acidity of adjacent epoxide C–H bonds should not be surprising, in view of their electronegative character. But electronegativity cannot be invoked as the determining factor for epoxides bearing the Ph_3Si or Me_3Si group; the electron-releasing silicon (Pauling electronegativity of 1.90 versus 2.55 for carbon) would be expected to have the reverse effect on the

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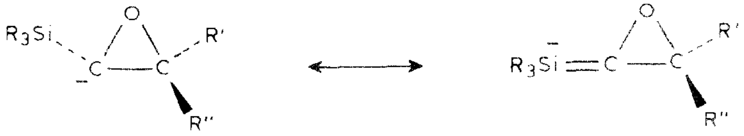
* The lack of stereoselectivity in this fluorodesilylation suggests that an enolate intermediate is involved and thus the chirality at the epoxide carbon is lost.

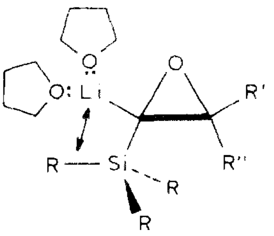
C–H bond. To explain the observed acidity, some kind of electron withdrawal by silicon must be invoked, in order to remove electron density from the C–H bond or to stabilize the carbanion after proton loss (XXVIa, XXVIb).



(XXVIa) (XXVIb)

The above-depicted resonance description would delocalize some charge onto silicon; a molecular orbital account would ascribe such delocalization to overlap of the carbanion's sp^n orbital with the vacant silicon *d*-orbitals or the antibonding σ-C–Si orbitals [14,15]; and Fajans' polarizability treatment would view the electron cloud about silicon as readily deformable by the adjacent negative charge [16].

Although no decisive choice can be made from among these theories, some experimental observations are noteworthy. First, since lithiation occurs with retention of configuration, much double-bond character between silicon and carbon, as implied by XXVIb, is unlikely, for this interaction would favor epimerization at the epoxide carbon. Secondly, since donor solvents are necessary for these lithiations, these lithio-epoxides are undoubtedly solvated (XXVII). In light of this, it is difficult to see how the R–Si and C–Li bonds could approach each other to realize the overlap of the filled C–Li and the empty, antibonding R–Si orbitals. Steric hindrance to proper allignment would appear to be great. Possibly Fajans' polarizability theory may therefore bear closer scrutiny in explaining this unusual acidity of silyl epoxides.



(XXVII)

As to the thermal stability of these α-heterosubstituted lithio-epoxides, this behavior may also be related to their steric character. The placement of bulky substituents α to the C–Li should retard the usual auto-association of RLi units into dimers, tetramers or hexamers. It is likely that just such auto-association is the pathway for the decomposition of the lithium reagents depicted in Schemes 1 and 2.

Experimental

Starting materials

Heterosubstituted olefins

(1) Olefins synthesized by known procedures. The methods cited were used to prepare the following: trimethyl(vinyl)silane [17]; triphenyl(vinyl)silane [17] and its vinyl-deuteriated isomers [11]; *cis*- and *trans*-isomers of trimethyl(β-styryl)silane [18]; trimethyl(*cis*-1-octenyl)silane [19]; triphenyl(vinyl)tin [20]; tri-n-butyl(*cis*-β-

styryl)tin [21]; phenyl *trans*-β-styryl sulfone [22]; and diethyl vinylphosphonate [23].

(2) Original olefin syntheses. (a) trans-1-Octenyl(triphenyl)silane (IX). To a solution of 11.0 g (0.1 mol) of 1-octyne in 14.2 g (0.105 mol) of trichlorosilane was added 0.1 ml of a solution of 50 mg of chloroplatinic acid dissolved in 1.0 ml of 2-propanol. The reaction mixture was heated to reflux, at which temperature the reaction exotherm maintained the mixture for some time. After 60 min the mixture was cooled and allowed to stand 12 h. The reaction mixture was heated for 2 h, cooled and then finally subjected to distillation. After a forerun the main fraction of trichloro(*trans*-1-octenyl)silane was collected at 74–75 °C (0.1 mmHg), 22.5 g (92%); ^{1}H NMR (neat) 0.4–2.13 (m, 15H), 5.6 (m, 1H) and 6.2–6.7 (m, 1H). Anal. Found: C, 39.54; H, 5.93. $C_8H_{15}Cl_3Si$ calcd.: C, 39.12; H, 6.15%.

Phenylmagnesium bromide was prepared from 41 g (0.3 mol) of bromobenzene and 7.29 g (0.3 g-atom) in 250 ml of anhydrous THF. Then 22.3 g (0.09 mol) of the above trichlorosilane which contained a small content of trichloro(2-octenyl)silane, was added dropwise to the above Grignard solution and the resulting mixture heated under reflux for 20 h. After quenching with aqueous NH_4Cl the separated organic layer was dried over anhydrous $MgSO_4$, the volatiles removed by evaporation and the residue subjected to column chromatography on neutral alumina by using benzene-hexane (v/v 1/20) as the eluent. The yield of IX was 27 g (86%); recrystallization from 2-propanol gave colorless product, m.p. 56–58 °C; ^{1}H NMR (CCl_4) 0.8–2.4 (m, 13H), 6.15 (br s, 2H) and 7.1–7.7 (m, 15H). Anal. Found: C, 84.37; H, 8.25. $C_{26}H_{30}Si$ calcd.: C, 84.26; H, 8.16%.

(b) trans-1-Octenyl phenyl sulfone (XXIV). A mixture of 39.2 g (0.35 mol) of 1-octene, 53.0 g (0.3 mol) of phenylsulfonyl chloride, 1.11 g (9 mmol) of triethylammonium chloride and 830 mg (6 mmol) of copper(II) chloride in 12 ml of acetonitrile was heated at incipient reflux for 35 h. The cooled reaction mixture was diluted with 500 ml of CH_2Cl_2 and then treated dropwise with 36 g of triethylamine. The mixture was heated to reflux for 60 min and then admixed with aqueous HCl (10 ml of concentrated HCl and 100 ml of H_2O). The phases were separated, the aqueous phase extracted with $CHCl_3$ and the combined organic phases washed with water. The dried ($MgSO_4$) organic layer was freed of volatile matter and the residue was subjected to chromatography on basic alumina, using benzene/hexane (v/v 2/3) as the eluent. The main fractions were then distilled to provide 37 g (49%) of XXIV, b.p. 170–172 °C (0.1 mmHg); ^{1}H NMR (CCl_4) 0.7–2.3 (m, 13H), 6.15 (d, 1H, J 18 Hz), 6.5–7.1 (m, 1H) and 7.2–7.8 (m, 5H). Anal. Found: C, 66.78; H, 7.85. $C_{14}H_{20}O_2S$ calcd.: C, 66.63; H, 7.99%.

(c) Tri-n-butyl(trans-1-octenyl)tin (XIX). According to published directions [24], *trans*-1-iodooctene was prepared (24.5 g, 65%, b.p. 65 °C (0.1 mmHg). A solution of 22.5 g (95 mmol) of this iodo compound in 300 ml of THF, 75 ml of ethyl ether and 75 ml of hexane was cooled to -95 to -105 °C and then treated dropwise with 102 ml of 1.86 *M* t-butyllithium in pentane. The mixture was allowed to warm up to -80 °C and after 20 min recooled to -95 °C. A solution of 30 g (90 mmol) of tri-n-butyltin chloride in 50 ml of THF was then slowly introduced. After the mixture was allowed to warm to 0 °C and quenched with water, the organic layer was separated, dried and evaporated to give 36 g ($\sim$ 99%) of crude XIX, which was quite pure by ^{1}H NMR spectroscopy. Column chromatography on neutral alumina gave an analytical sample: ^{1}H NMR (CCl_4) 0.7–2.2 (m, 40H) and 5.78–5.92 (m, 2H). Anal. Found: C, 59.58; H, 10.82. $C_{20}H_{42}Sn$ calcd.: C, 59.87; H, 10.55%.

Epoxides

(1) Known epoxides. The silyl-substituted olefins were converted into epoxides with *m*-chloroperbenzoic acid [11]. Phenyl *trans*-β-styryl sulfone was epoxidized with basic hydrogen peroxide (cf. infra).

(2) Other epoxides. (a) Epoxyethyl(triphenyl)tin (XVIII). A solution of 29.8 g (79 mmol) of triphenyl(vinyl)tin and 15.7 g (85%, 79 mmol) of *m*-chloroperbenzoic acid in 120 ml of chloroform was allowed to stand for 20 h at 20–25 °C. The precipitated *m*-chlorobenzoic acid was filtered off and washed with pentane. The combined pentane/chloroform extracts were evaporated and the residue chromatographed on silica gel with hexane as the initial eluent. With this elution 16 g of starting material was recovered. Further elution with ether/hexane (v/v 1/18) yielded XVIII. Recrystallization gave the pure epoxide, m.p. 89–91 °C, 48% based on unrecovered starting material: ^{1}H NMR (CCl_4) 2.55–3.15 (m, 3H) and 7.1–7.6 (m, 15H). Anal. Found: C, 61.09; H, 4.81. $C_{20}H_{18}OSn$ calcd.: C, 61.12; H, 4.62%.

(b) Tri-n-butyl(cis-epoxystyryl)tin (attempted). A similar procedure to that described above led to no detectable epoxide; column chromatography on silica gel gave only styrene with a hexane eluent and perhaps some tri-n-butyl *m*-chlorobenzoate with the ether/hexane eluent.

(c) Tri-n-butyl(trans-1,2-epoxy-1-octyl)tin (XIXa). A solution of 4.0 g (10 mmol) of XIX and 1.98 g (85%, 10 mmol) of *m*-chloroperbenzoic acid in 15 ml of chloroform was prepared below 10 °C, so as to avoid a temperature rise. A stirring period of 12 h at 10 °C was terminated by dilution with pentane and filtration of the suspension. The filtrate was washed successively with aqueous solutions of $NaHCO_3$, $NaHSO_3$ and finally $NaHCO_3$. Column chromatography as in section (a) gave 3.5 g of pure epoxide (83%); ^{1}H NMR (CCl_4) 0.7–1.7 (m, 40), 2.3 (d, *J* 4.0 Hz) and 2.7 (m).

Anal. Found: C, 57.50; H, 10.34. $C_{20}H_{42}OSn$ calcd.: C, 57.57; H, 10.15%.

A repetition of the reaction on an 80 mmolar scale gave 61% of the epoxide and some isolated 1-octene.

(d) trans-1,2-Epoxy-1-octyl(triphenyl)silane (XIa). A solution of 6.92 g (20 mmol) of XI and 2.87 g (85%, 20 mmol) of *m*-chloroperbenzoic acid in 25 ml of chloroform was allowed to react for 20 h at 20–25 °C and 2.5 h at reflux. Usual workup and column chromatography on silica gel gave the epoxide, which after recrystallization from 2-propanol melted at 63–65 °C, 4.9 g (98%, considering 1.9 g of XIa recovered); ^{1}H NMR (CCl_4) 0.8–1.7 (m, 13H), 2.5–2.7 (m, 2H) and 7.15–7.7 (m, 15H). Anal. Found: C, 65.52; H, 6.17. $C_{26}H_{30}OSi$ calcd.: C, 65.44; H, 6.34%.

(e) cis-1,2-Epoxy-1-octyl(trimethyl)silane (VIIIa). The dissolution of 7.38 g (40 mmol) of VIII and 8.13 g (85%, 40 mmol) of *m*-chloroperbenzoic acid in 60 ml of $CHCl_3$ resulted in an exotherm that was moderated by external cooling. After stirring for 72 h at 20–25 °C the mixture was diluted with benzene and the organic solution washed successively with aqueous $NaHCO_3$, $NaHSO_3$ and finally $NaHCO_3$ solutions. Drying over anhydrous Na_2SO_4 and evaporation in vacuo gave 7.2 g of crude product, which was chromatographed on silica gel, with a hexane eluent, to provide 6.1 g of pure epoxide VIIIa (76%); ^{1}H NMR (CCl_4) 0.8 (s, 9H), 0.8–2.5 (m, 14H) and 2.5 (m, 1H). Anal. Found: C, 65.78; H, 12.23. $C_{11}H_{24}OSi$ calcd.: C, 65.93; H, 12.07%.

(f) trans-1,2-Epoxy-1-octyl phenyl sulfone (XXIVa). A solution of 13.7 g (54 mmol) of XXIV, 22 ml of 2.2 *M* aqueous NaOH, 30 ml of 30% H_2O_2 and 150 ml of

acetone was stirred vigorously for 60 min at 40 ° C and 90 min at 50 ° C. Evaporation of the volatile matter and column chromatography of the residue on neutral alumina gave, by eluting with benzene-hexane (v/v 1/1), 8.2 g of XXIVa, 60% as an oil; ^{1}H NMR (CCl_4) 0.6–1.07 (m, 13H), 3.25–3.5 (m, 1H), 3.73–3.87 (d, 1H) and 6.9–7.77 (m, 5H). Anal. Found: C, 62.53; H, 7.76. $C_{14}H_{20}O_3S$ calcd.: C, 62.66; H, 7.51%.

(g) Diethyl epoxyethylphosphonate (XXIIa). A solution of 42.7 g (0.26 mol) of XXII, 26 g (90%, 0.26 mol) of t-butylhydroperoxide and 2 ml of Triton B (40% in methanol) was prepared in 150 ml of benzene at 0 ° C. The solution was allowed to warm to 20–25 ° C over 12 h. Then 1.0 ml of Triton B added and the solution was slowly warmed to 60 ° C. Some NaOH pellets were added to basify the mixture and the solution stirred for 48 h. Evaporation of volatile matter and distillation through a Vigreux column at 0.1 mmHg gave starting material, 15 g, b.p. 35–40 ° C, followed by a fraction composed of the desired epoxide and the ether, t-$BuOCH_2CH_2PO(OEt)_2$. Redistillation of this fraction gave pure XXIIa, b.p. 56–60 ° C, 8.5 g (31%); ^{1}H NMR (CCl_4) 1.33 (t, 6H), 2.90 (t of t, 3H) and 4.07 (q, 4H). Anal. Found: C, 40.22; H, 6.98. $C_6H_{13}O_4P$ calcd.: C, 40.00; H, 7.27%.

Organometallic reagents

t-Butyllithium in pentane solution and n-butyllithium in hexane were purchased from Aldrich Chemical Company and were analyzed just before use by the Gilman double-titration procedure [18]. Organoaluminum reagents were kindly provided by Texas Alkyls, Inc.

Reaction media for organometallic reactions (diethyl ether, tetrahydrofuran, toluene and methylene chloride) were purified by standard procedures [18] and then made anhydrous and deoxygenated by final distillation from appropriate drying agents [18] under an argon atmosphere.

Instrumentation and analyses

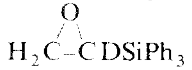
All melting points were measured with a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on Perkin–Elmer spectrophotometers. Models 457 and 283B, which were equipped with sodium chloride optics. Proton magnetic resonance spectra (^{1}H NMR) were obtained with a Varian spectrometer, Model EM-360, on pure samples or on 10% solutions in pure deuterated solvents. The ^{1}H NMR data are reported on the δ-scale in parts per million with reference to internal tetramethylsilane, followed by peak multiplicities, relative proton intensities and coupling constants in hertz. Mass spectral data (MS) were collected either with a Dupont instrument, Model 21-491B, or with a MS-902/CIS.2 instrument. The latter spectrometer was provided with a V6 Datasystem 2040 computerized recorder.

Gas-liquid phase chromatographic analyses (GC) were carried out with an F&M temperature-programmed chromatograph, Model 720, equipped with dual 12-ft columns of a 10% UC-298 phase on a Chromosorb W support and with an electronic peak-area integrator. Thin layer chromatographic analyses (TLC) were done on Eastman Chromagram Sheets, no. 13181, consisting of silica gel with fluorescent indicator. Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

General procedures

All steps in the preparation, transfer and main reactions of the organometallic reagents studied here were conducted under an atmosphere of anhydrous and oxygen-free argon. All solvents and apparatus were likewise freed of traces of dissolved or adsorbed moisture and oxygen and then maintained under argon. Methods and techniques for working under anhydrous and anaerobic conditions have been described previously [18].

Lithiation of epoxyalkylsilanes

Epoxyethyl(triphenyl)silane (VIa). (1) A solution of 302 mg (1 mmol) of VIa in 10 ml of THF was cooled to −78 °C and treated with 2 ml of 2.4 *M* n-butyllithium in hexane. After 4 h at this temperature 2.0 ml of D_2O (99%) was added and stirring continued for 15 min at −78 °C. After warming to 25 °C, CH_2Cl_2 was added and the solution dried over anhydrous Na_2SO_4. Removal of the solvent gave 287 mg of the epoxide, m.p. 74–76 °C, whose ^1H NMR spectrum showed the complete absence of the proton *α*- to the silicon and the oxygen. Hence, complete conversion to  $H_2C(O)CDSiPh_3$ had been achieved.

(2) In an analogous reaction with *cis*-1,2-dideuterioepoxyethyl(triphenyl)silane (VIIa) followed by quenching with H_2O, the recovered epoxide, m.p. 73–75 °C, was shown by ^1H NMR spectroscopy to be entirely *trans*-2-deuterioepoxyethyl(triphenyl)silane. Therefore, the *α*-deuterium had been completely replaced by a proton with retention of configuration (^1H NMR (CCl_4) 2.45 (m of 4 Hz width 1H) and 2.85 (d, J_{trans} 4.2 Hz, 1 H)).

(3) A solution of 302 mg (1 mmol) of VIa in 20 ml of THF was treated with 4.8 mmol of n-butyllithium in hexane at −78 °C and the mixture then allowed to warm up to 25 °C over 1 h. The cherry-red solution was quenched with water and worked up as usual. Column chromatography on neutral alumina and elution with hexane gave 1.25 g (73%) of 2-hexenyl(triphenyl)silane (XIII) and 0.24 g (15%) of n-butyl(triphenyl)-silane (XIV) (cf. infra); ^1H NMR (CCl_4) of XIII: 0.55–1.6 (m, 7H), 2.1–2.5 (m, 2H), 5.5–5.65 (br d, 1H), 5.90–6.00 (m, 1H) and 7.1–7.65 (m, 15H).

Anal. Found: C, 84.10; H, 7.81. $C_{24}H_{26}Si$ calcd.: C, 84.15; H, 7.65%.

(4) A solution of 302 mg (1 mmol) of VIa in 20 ml of hexane was treated with 4.8 mmol of n-butyllithium in hexane at 25 °C and the reaction mixture heated at reflux for 30 min. Usual workup and examination of the organic residue by ^1H NMR spectroscopy showed no starting material (VIa), a trace of 2-hexenyl(triphenyl)silane (XIII) and the preponderance of n-butyl(triphenyl)silane (XIV). This latter component was recrystallized from methanol to give 180 mg (69%) of pure XIV, m.p. 86–88 °C; ^1H NMR ($CDCl_3$) 0.4–1.1 (m, 3H), 1.1–1.7 (br s, 6H) and 6.7–7.0 (m, 15H). Anal. Found: C, 85.19; H, 5.80. $C_{22}H_{18}Si$ calcd.: C, 85.11; H, 5.84%.

An authentic sample of XIV was prepared in 64% yield from chloro(triphenyl)silane and n-butylmagnesium chloride in refluxing THF; m.p. 87–89 °C.

(5) A solution of 302 mg (1 mmol) of VIa in 20 ml of THF and 4.8 mmol of n-butyllithium in hexane were allowed to react at −78 °C for 4 h. Then 12 ml of a 1.1 *M* ethereal solution of phenyllithium was introduced and the mixture allowed to warm to room temperature. The deep red mixture was quenched with water and worked up in the usual way. The ^1H NMR spectrum of the crude product showed

the presence of about 80% of triphenyl(1-phenyl-1-ethenyl)silane (XV), (doublets at 5.65 and 6.20 ppm, J 3 Hz). This product could be isolated as crystals from hexane, m.p. 129–131° C (65%); lit. [25] m.p. 129–130° C.

(6) A solution of 302 mg (1 mmol) of VIa in 10 ml of THF and 0.15 ml of TMEDA at −78° C was treated with 1.2 mmol of n-butyllithium in hexane. After 40 min at −78° C the reaction mixture was quenched with D_2O. Workup and ^1H NMR spectral analysis showed the recovered epoxide to be exclusively and completely converted to 1-deuterioepoxyethyl(triphenyl)silane.

Epoxytrimethylsilane (Va). A solution of 7.2 ml (45 mmol) of Va, 7.2 ml (57 mmol) of chloro(trimethyl)silane and 6.3 ml (51 mmol) of TMEDA in 300 ml of pentane was cooled to −95° C and then treated with 26.6 ml of 1.86 M t-butyllithium in pentane over 45 min. The t-butyllithium appeared to react as soon as it was added, since the bright yellow color of the t-BuLi-TMEDA complex did not appear. Usual workup and distillation at 15 mmHg yielded a fraction between 65 ± 70° C that was the expected 1,1-bis(trimethylsilyl)epoxyethane, 6.3 g (75%); ^1H NMR (CCl_4) 0.2 (s, 18H) and 2.82 (s, 2H). Anal. Found: C, 51.22; H, 10.76. $C_8H_{20}OSi_2$ calcd.: C, 51.00; H, 10.70%.

Repetition of the reaction described above, with the introduction of 1.5 molar equivalents of *N,N*-diethylbenzamide (with respect to equivalents of epoxide Va), gave upon workup and distillation a fraction boiling at 55° C (0.1 mmHg) which was a 65% yield of 1-benzoylepoxyethyl(trimethyl)silane; ^1H NMR (CCl_4) 0.19 (s, 9H), 2.88 (d, 2H), 7.2–7.4 (m, 3H) and 7.78–7.95 (m, 2H). Anal. Found: C, 65.63; H, 7.09. $C_{12}H_{16}O_2Si$ calcd.: C, 65.41; H, 7.32%.

cis-Epoxystyryl(trimethyl)silane (Xa). A solution of 1.92 g (10 mmol) of X, 1.77 ml (14 mmol) of chloro(trimethyl)silane and 1.4 ml (11 mmol) of TMEDA in 100 ml of pentane was cooled to −78° C and treated with t-butyllithium (11 mmol in pentane) over 30 min. The mixture was allowed to warm to 0° C before being quenched by water. The crude organic residue obtained by the usual workup was chromatographed on silica gel with the aid of hexane as the initial eluent. Thereafter, an ether/hexane eluent (v/v 1/18) gave the main product, *trans*-1,2-bis(trimethylsilyl)epoxystyrene, 83%, which appeared to contain a small amount of 1,1-bis(trimethylsilyl)epoxystyrene). Anal. Found: C, 63.59; H, 9.27. $C_{14}H_{24}OSi_2$ calcd.: C, 63.57; H, 9.14%.

trans-Epoxystyryl(trimethyl)silane (XIa). A solution of 1.92 g (10 mmol) of XIa, 1.77 ml (14 mmol) of chloro(trimethyl)silane and 1.4 ml (11 mmol) of TMEDA in 100 ml of pentane was cooled to −78° C and treated with t-butyllithium (11 mmol in pentane) over 30 min. The reaction mixture was warmed to −50° C and quenched with water. Usually workup and ^1H NMR analysis of the organic residue showed the presence of about a 1/1 mixture of starting XIa and what appeared to be a trimethylsilyl derivative of XIa, possibly on the CH_3Si group, *trans*-epoxystyryl(dimethyl)trimethylsilylmethylsilane (XII).

cis-1,2-epoxy-1-octyl(trimethyl)silane (VIIIa). A solution 1.2 g (6 mmol) of VIIIa, 1.2 ml of TMEDA and 60 ml of hexane was cooled to −95° C and then treated with 9.67 mmol of t-butyllithium in pentane. After 75 min at −80 to −90° C the mixture was quenched with D_2O (10 ml in 50 ml of THF). Usual workup and chromatography on silica gel with hexane and with ether/hexane (v/v 1/9) gave 950 mg of starting VIIIa (79%), which was completely deuteriated α to the silicon and the oxygen.

trans-1,2-Epoxy-1-octyl(triphenyl)silane (IXa). When 362 mg (1 mmol) of IXa in 10 ml of THF was treated with 1.48 mmol of n-butyllithium in hexane for 2 h at −78 °C and quenched with D_2O, the recovered epoxide was undeuteriated.

Treatment of 181 mg (0.5 mmol) of IXa and 0.15 ml of TMEDA in 10 ml of hexane with 1.2 ml of 1.48 *M* n-butyllithium in hexane at −78 °C gave a suspension. The mixture was permitted to warm up until it became homogeneous and was recooled to −78 °C. A solution of 1 ml of D_2O in 10 ml of THF was then added. Workup yielded the starting epoxide, which by ^{1}H NMR spectroscopy was shown to be partially deuteriated (~50%) α to the silicon and the oxygen.

Lithiation of epoxyalkyltins

Epoxyethyl(triphenyl)tin (XVIIIa). To 10 ml of 1.0 *M* phenyllithium in ether, which was cooled to −78 °C, was added dropwise a solution of 786 mg (2 mmol) of XVIIIa in 10 ml of ether. The solution turned bright yellow-orange upon initial admixing and the color faded rapidly. After the solution was allowed by warm to 0 °C, it was quenched with water and CH_2Cl. The dried, separated organic layer was concentrated to precipitate tetraphenyltin, 607 mg (71%), m.p. 226–228 °C. The residual, pentane-soluble fraction yielded a minimum of 33% of styrene.

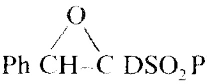
Tri-n-butyl(trans-1,2-epoxy-1-octyl)tin (XIXa). The epoxide XIXa (833 mg, 2 mmol) in 15 ml of hexane was cooled to −100 °C and the n-butyllithium in hexane (2.2 mmol) then introduced. The mixture was warmed to −85 °C over 15 min and then recooled. Quenching with D_2O and workup yielded only starting material.

A similar reaction that substituted 15 ml of THF for hexane led, upon workup, to a crude organic residue that was essentially pure tetra-n-butyltin.

Finally, a reaction was conducted as follows: 833 mg (2 mmol) of epoxide XIXa was dissolved in 16 ml of THF, 4 ml of ether and 4 ml of pentane and then cooled to −95 °C. t-Butyllithium (6.6 mmol) in pentane was added and the mixture gradually allowed to warm to 0 °C. Usual workup and careful removal of the solvent from the organic phase permitted the isolation by gas chromatography of *trans*-2,2-dimethyl-3-decene; 40% yield; IR (neat) 980 cm^{-1} (*trans*-CH=CH); ^{1}H NMR (neat) 0.85 (s, 3H), 0.95 (s, 9H), 1.27 (br, 8H), 1.90 (br, 3H, 5.29 (apparent t, 2H).

The less volatile component in the gas chromatogram was tri-n-butyl(t-butyl)tin; ^{1}H NMR (neat) 1.08 (s, 9H) and 0.50–1.70 (m, 27H); IR (neat) nothing but CH absorptions between 1600 and 4000 cm^{-1}. This compound was identical with an authentic sample made from t-butyllithium and chloro(tri-n-butyl)tin in THF; b.p. 100–102 °C (0.1 mmHg).

Lithiation of epoxyalkyl sulfones

trans-Epoxystyryl phenyl sulfone (XXIIIa). A solution of 520 mg (2 mmol) of XXIIIa dissolved in a mixture of 24 ml of THF, 6 ml of ethyl ether and 4 ml of hexane was chilled to −110 °C and then treated with 2.0 ml of 1.48 *M* n-butyllithium in hexane. After 45 min between −90 and −110 °C the reaction mixture was quenched with 2 ml of D_2O. The usual workup gave the crude product as a yellow solid, whose ^{1}H NMR spectrum showed the disappearance of the upfield epoxide ring proton. Recrystallization from 95% ethanol gave 360 mg (69%) of the α-deuterio derivative of XXIIIa  $\mathrm{Ph\,CH{-}C\,DSO_2Ph}$ (with $\overset{O}{\wedge}$ bridging CH–C), m.p. 102–104 °C.

trans-1,2-Epoxy-1-octyl phenyl sulfone (XXIVa). A solution of 276 mg (1.0 mmol) of XXIVa in 6 ml of THF and 2 ml of ethyl ether was cooled to −100 °C and then treated with 0.8 ml of 2.3 *M* n-butyllithium in hexane. After 45 min between −90 and −100 °C the mixture was quenched with 2 ml of D_2O in 5 ml THF. Usual workup gave 264 mg (96%) of recovered epoxide whose ^1H NMR spectrum showed no doublet signal at 3.90 ppm. Hence, XXIVa was deuterated at epoxide carbon α to the sulfonyl group.

Lithiation of diethyl epoxyethylphosphonate (XXIIa)

A solution of 1.08 g (6 mmol) of XXIIa and 1.14 ml (9 mmol) of chloro(trimethyl)silane dissolved in 18 ml of THF, 4 ml of ether and 4 ml of hexane was cooled to −115 °C and then treated with 8.3 mmol of lithium diisopropylamide in 6 ml of THF and 5 ml of hexane (generated from diisopropylamine (8.3 mmol) and 8.3 mmol of n-butyllithium in hexane) over 40 min. After an additional 15 min the solution was allowed to warm to 0 °C and then quenched with 3 ml of water. The usual workup and the removal of volatiles under reduced pressure gave the crude trimethylsilyl derivative in 91% yield (1.85 g). Distillation yielded 1.72 g (84%) of diethyl 1-trimethylsilylepoxyethylphosphonate, b.p. 115–120 °C (0.1 mmHg); ^1H NMR (CCl_4) 0.03 (s, 9H), 1.2–1.5 (t, 6H), 2.65–3.2 (m, 2H) and 3.8–4.3 (m, 4H).

Anal. Found: C, 42.76; H, 8.50. $C_9H_{21}O_4PSi$ calcd.: C, 42.84; H, 8.39%.

Derivatives of α-heterosubstituted epoxides via lithiation

Methylation. (1) Epoxyethyl(triphenyl)silane (VIa). A solution of 1.21 g (4 mmol) of VIa in 20 ml of THF was treated at −78 °C with 7.2 mmol of n-butyllithium in hexane. After 2 h at −78 °C 1.7 ml (15 mmol) of methyl iodide was introduced. Usual workup gave a crude product that was recrystallized from methanol. 1.10 g of 1-methylepoxyethyl(triphenyl)silane (91%), m.p. 113–114.5 °C; ^1H NMR (CCl_4) 1.40 (s, 3H), 2.51 (s, 2H) and 7.2–7.6 (m, 15H). Anal. Found: C, 79.65; H, 6.48. $C_{21}H_{20}OSi$ calcd.: C, 79.70; H, 6.37%.

(2) cis-1,2-Epoxy-1-octyl(trimethyl)silane (VIIIa). A solution of 1.0 g (5 mmol) of epoxide VIIIa and 1.0 ml of TMEDA in 50 ml of hexane was treated at −95 °C with 3.5 ml of 2.3 *M* t-butyllithium in pentane. After 75 min between −80 and −90 °C the mixture was cooled to −100 °C and 1.25 ml (20 mmol) of methyl iodide in 50 ml of THF added over 15 min. Over 75 min the solution was allowed to reach 0 °C and then quenched with water. Usual workup and chromatography on silica gel, first with hexane and then with ether/hexane (v/v 1/9) gave 870 mg of the pure 1-methyl derivative of VIIIa (81%); ^1H NMR (CCl_4) 0.08 (s, 9H), 0.8–2.5 (m, 16H) and 2.45 (m, 1H).

Anal. Found: C, 67.41; H, 11.94. $C_{12}H_{26}OSi$ calcd.: C, 67.22; H, 12.22%.

(3) trans-Epoxystyryl phenyl sulfone (XXIIIa). A solution of 1.04 g (4 mmol) of XXIIIa in 24 ml of THF and 6 ml of ethyl ether were treated at −90 to −110 °C with 3.4 ml of 1.48 *M* n-butyllithium in hexane and the mixture held at −95 °C for 60 min. Methyl iodide (1.42 g, 10 mmol) was added and the temperature kept at −95 °C for 15 min and then warmed to −20 °C. Usual aqueous quench and the workup provided a crude product containing no starting epoxide. Recrystallization from 95% ethanol (−35 °C) gave 675 mg (62%) of 1-methyl derivative of XXIIIa, m.p. 111–113 °C; ^1H NMR (CCl_4) 1.27 (s, 3H), 4.76 (s, 1H), 7.28 (s, 5H) and 7.45–8.05 (m, 5H). Anal. Found: C, 65.60; H, 5.10. $C_{15}H_{14}O_3S$ calcd.: C, 65.67; H, 5.14%.

(4) trans-1,2-Epoxy-1-octyl phenyl sulfone (XXIVa). The lithiation of XXIVa (1.10 g) was conducted in the manner described above. The methyl iodide (2.13 g, 15 mmol) was introduced at −95 °C and the mixture allowed to warm. The crude product, 1.12 g (96%), was essentially the pure 1-methyl derivative by ^{1}H NMR spectroscopy (CCl_4) 0.83–1.41 (m, 16H), 3.40–3.70 (m, 1H) and 6.94–7.70 (m, 5H). A sample was chromatographed on silica gel for analysis. Anal. Found: C, 64.05; H, 7.66. $C_{15}H_{22}O_3Si$ calcd.: C, 63.80; H, 7.85%.

(5) Diethyl epoxyethylphosphonate (XXIIa). This epoxide was lithiated on a 5 mmolar scale by lithium diisopropylamide in the manner described above, except that 15 mmol of methyl iodide was present with the epoxide as the LDA was slowly added. Usual workup gave 720 mg of crude 1-methylated product (74%). Distillation in a bulb-to-bulb apparatus gave 550 mg (57%) of diethyl 1-methylepoxyethylphosphonate, ^{1}H NMR (CCl_4) 1.15–1.5 (overlapping singlet and triplet, 9H), 2.6–3.1 (m, 2H) and 3.85–4.3 (m, 4H). Anal. Found: C, 43.38; H, 7.82. $C_7H_{15}O_4P$ calcd.: C, 43.30; H, 7.79%.

Acylation. (1) Epoxyethyl(triphenyl)silane (VIa). A solution of 906 mg (3 mmol) of VIa in 15 ml of THF was treated at −78 °C with 3.6 mmol of n-butyllithium. After 3 h at −78 °C 583 mg (4 mmol) of *N*-benzoylaziridine was added. Usual workup and crystallization of crude product from CH_2Cl_2 ethanol gave 955 mg (78%) of 1-benzoylepoxyethyl(triphenyl)silane, m.p. 145–146 °C. Anal. Found: C, 79.63; H, 5.57. $C_{27}H_{22}O_2Si$ calcd.: C, 79.76; H, 5.46%.

The use of *N,N*-diethylbenzamide as the benzoylating agent gave comparable yields.

In a similar manner, the lithio derivative of VIa could be treated with *N,N*-dimethylacetamide (100% excess) to give 72% of 1-acetylepoxyethyl(triphenyl)silane, m.p. 115–117 °C (from hexane); ^{1}H NMR (CCl_4) 1.83 (s, 3H), 2.65–2.90 (d of d, 2H) and 7.0–7.5 (m, 15H). Anal. Found: C, 76.80; H, 5.59. $C_{22}H_{20}O_2Si$ calcd.: C, 76.71; H, 5.85%.

(2) cis-Epoxystyryl(trimethyl)silane (Xa). Lithiation of this epoxide (10 mmol), as described above, and treatment with *N,N*-diethylbenzamide (14 mmol) gave a crude product, upon the usual hydrolytic workup, that was chromatographed on silica gel. Elution with ether/hexane (v/v 1/30) gave some starting Xa (20%), and then fairly pure benzoylated Xa 2.4 g (80%). Bulb-to-bulb distillation provided the analytically pure oil, the benzoyl derivative α to the phenyl in Xa; ^{1}H NMR (CCl_4) 0.2 (s, 9H), 2.98 (s, 1H) and 7.6–8.3 (m, 10H). Anal. Found: C, 72.91; H, 6.94. $C_{18}H_{20}O_2Si$ calcd.: C, 72.93; H, 6.80%.

(3) cis-1,2-Epoxy-1-octyl(trimethyl)silane (VIIIa). Lithiation of this epoxide (10 mmol), as described above, and treatment with *N,N*-dimethylacetamide (25 mmol) gave 94% of the crude acetyl derivative of VIIIa, which after chromatography on silica gel was analytically pure; ^{1}H NMR (neat) 0.11 (s, 9H), 0.75–1.7 (m, 13H), 1.82 (s, 3H) and 2.75–3.0 (m, 1H). Anal. Found: C, 63.90; H, 10.75. $C_{13}H_{26}O_2Si$ calcd.: C, 63.58; H, 10.81%.

Silylation. (1) Epoxyethyl(triphenyl)silane (VIa). Lithiation of this epoxide on a 3-mmolar scale by the method given in section 1 under Lithiations, followed by quenching with 5 mmol of Me_3SiCl and then water, gave after chromatography on silica gel 79% of pure 1-trimethylsilylepoxyethyl(triphenyl)silane, m.p. 75–76 °C (from MeOH); ^{1}H NMR (CCl_4) 0.2 (s, 9H), 3.18 (s, 2H) and 7.7–8.6 (m, 15H). Anal. Found: C, 73.79; H, 6.66. $C_{23}H_{26}OSi_2$ calcd.: C, 73.74; H, 6.70%

(2) trans-Epoxystyryl phenyl sulfone (XXIIIa). This epoxide was lithiated on a 30-mmolar scale and then treated with 50 mmol of Me_3SiCl. Usual workup and recrystallization from MeOH gave 76% of the pure trimethylsilyl derivative α to the phenyl in XXIIIa; m.p. 95–97 °C. Anal. Found: C, 61.48; H, 6.15. $C_{17}H_{20}O_3SSi$ calcd.: C, 61.41; H, 6.06%.

Other derivatives. (1) Trimethylstannyl. Epoxyethyl(triphenyl)silane was lithiated on a 2-mmolar scale by the method given in section 1 and then treated with 2.4 mmol of Me_2SnCl. Usual workup and recrystallization of the crude product from MeOH, gave 55% of pure 1-trimethylstannylepoxyethyl(triphenyl)silane, m.p. 77–79 °C; ^1H NMR (CCl_4): −0.19 (s, 9H), 2.90 (s, 2H) and 7.2–7.8 (m, 5H). Anal. Found: C, 59.32; H, 5.77. $C_{23}H_{26}SiSn$ calcd.: C, 59.38; H, 5.63%.

(2) n-Butyl. Epoxyethyl(triphenyl)silane was lithiated as above on a 10-mmolar scale and then treated with 12 mmol of 1-iodobutane. Usual workup and column chromatography gave 65% of the oily 1,2-epoxy-2-hexyl(triphenyl)silane; ^1H NMR (CCl_4) 0.7–2.5 (m, 13) and 7.1–7.5 (m, 15H).

(3) Carboxy. Epoxyethyl(triphenyl)silane was lithiated as above on a 2-mmolar scale. The mixture was treated with a stream of dry CO_2 at −78 °C and then allowed to warm to 25 °C. After acidification with dilute, aqueous HCl, the mixture was extracted into ether. The ether extracts were extracted, in turn with aqueous $NaHCO_3$; acidification of the aqueous extracts yielded 550 mg (70%) of 2,3-epoxy-2-triphenylsilylpropionic acid, m.p. 137–138 °C. Neutralization equiv. 346; theoretical: 345. ^1H NMR ($CDCl_3$) 2.0–2.6 (m, 2H), 6.9–7.4 (m, 15) and 9.5 (s, 1H).

Derivatizing reactions of heterosubstituted epoxides

Aluminum hydride reductions. (1) Epoxyethyl(triphenyl)silane (VIa). A solution of 604 mg (2 mmol) of VIa in 10 ml of hexane was mixed with 0.40 ml (2.2 mmol) of diisobutylaluminum hydride. The mixture became warm and was stirred for 60 min, whereupon the reaction was quenched with water. The organic layer was diluted with 50 ml of CH_2Cl_2, dried over anhydrous $MgSO_4$ and evaporated to give 525 mg (86%) of 2-triphenylsilylethanol, which upon recrystallization from hexane melted at 99–100 °C. Comparison with an authentic sample [13] confirmed its identity.

A similar reduction of 1-deuterioepoxyethyl(triphenyl)silane (VIIa) gave 93% of $Ph_3SiCHDCH_2OH$, m.p. 98–100 °C, as confirmed by ^1H NMR spectroscopy.

A similar reduction of epoxyethyl(triphenyl)silane with diisobutylaluminum deuteride [18] gave exclusively $Ph_3SiCHDCH_2OH$, m.p. 98–99 °C.

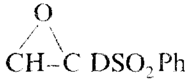
Finally, heating 1.0 mmol of the epoxide with 2.8 mmol of triethylaluminum in 15 ml of heptane for 19 h at reflux gave 55% of 2-triphenylsilylethanol, m.p. 99–100 °C (from hexane).

(2) 1-Methylepoxyethyl(triphenyl)silane. A solution of 326 mg (1.0 mmol) of this epoxide in 10 ml of hexane was treated at 25 °C with 0.25 ml (1.4 mmol) of $i\text{-}Bu_2AlH$. After 30 min, quenching with water and usual workup gave 323 g (99%) of alcohol. Recrystallization from hexane gave a m.p. of 153–155 °C and ^1H NMR ($CDCl_3$) showed it to be 2-triphenylsilyl-2-propanol: 1.20 (s, 1H), 1.50 (s, 6) and 7.2–7.9 (m, 15H). Anal. Found: C, 79.02; H, 7.05. $C_{21}H_{22}OSi$ calcd.: C, 79.19; H, 6.96%.

(3) trans-1,2-Epoxy-1-octyl(triphenyl)silane (IXa). A solution of 1.0 mmol of IXa and 0.36 ml (2.0 mmol) of $i\text{-}Bu_2AlH$ in 10 ml of hexane was heated at reflux for 60

min. Usual work-up gave the crude product (335 mg, 93%) that by ^{1}H NMR analysis was shown to be essentially pure n-$C_6H_{13}CHOHCH_2SiPh_3$.

(4) trans-Epoxystyryl phenyl sulfone (XXIIIa). A solution of 2 mmol of XXIIIa in 20 ml of hexane was treated at 25 °C with 1.1 ml (6 mmol) of i-Bu_2AlH. After the exotherm had subsided, the mixture was stirred for 30 min and quenched with water. Usual workup gave 250 mg of a foul-smelling oil; this proved to be 2-phenylethanol contaminated with phenyl mercaptan: ^{1}H NMR triplets at 2.67 and 3.63 ppm (J 7 Hz).



When $Ph\overset{O}{CH-C}DSO_2Ph$ was reduced in a similar manner, the product was $PhCH_2CHDOH$.

(5) cis-1-Methyl-2-phenylepoxyethyl phenyl sulfone. A similar reduction of this epoxide gave 1-phenyl-2-propanol: ^{1}H NMR (neat) 1.05 (d, 3H, J 6 Hz), 2.63 (d, 2H, J 6 Hz), 2.65 (s, 1H, disappears after D_2O treatment), 3.85 (sextet, 1H, J 6 Hz) and 7.1 (s, 5H).

(6) trans-1-Methyl-1,2-epoxy-1-octyl phenyl sulfone. This epoxide was reduced essentially quantitatively to 2-nonanol.

Fluorodesilylation of epoxyalkylsilanes. (1) 1-Benzoylepoxyethyl(triphenyl)silane. A solution of 1 mmol of this epoxide, 250 mg of KF and 228 mg of $PhCH_2NEt_3{}^+Cl^-$ in 10 ml of anhydrous acetonitrile stood at 25 °C for 15 h. The ^{1}H NMR spectrum of evaporated mixture showed no starting material, but had expected absorptions for benzoylepoxyethane (2.80, 2H, m and 3.95, 1H, d of d). The conversion was > 95%.

(2) 1,2-Epoxy-2-hexyl(triphenyl)silane. A solution of 5 mmol of this epoxide, 5 g of KF and 2.28 g of $PhCH_2NEt_3{}^+Cl^-$ in 20 ml of anhydrous dimethyl sulfoxide was stirred for 2 h at 20–25 °C. The reaction flask was connected through a reflux condenser to a tared cold trap. The pressure was reduced to 20 mmHg so that the DMSO refluxed and the product proceeded to the cold trap. After 4 h of such aspiration the cold trap's contents were analyzed by ^{1}H NMR spectroscopy. About a 65% yield of 1,2-epoxyhexane was obtained and identified by IR, GC and ^{1}H NMR analyses.

(3) 1-Acetyl-cis-1,2-epoxy-1-octyl(trimethyl)silane. A solution of 2 mmol of this epoxide 1.2 g of KF and 4.4 mmol of $PhCH_2NEt_3{}^+Cl^-$ in 20 ml of acetonitrile stood for 20 h at 20–25 °C. Usual workup revealed a quantitative desilylation but a 1/1 mixture of *cis*- and *trans*-isomers of 3,4-epoxy-2-decanone.

(4) 1-Methyl-cis-1,2-epoxy-1-octyl(trimethyl)silane. A solution of 6 mmol of this epoxide 1.5 g of $Et_4N^+F^-$ and 30 ml of anhydrous DMSO was stirred at 20–25 °C for 30 h. Usual workup revealed about 30% of remaining and 70% of *trans*-2,3-epoxynonane, which was separated by gas chromatography.

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