

Oxiranyl Anions and Aziridinyl Anions

Tsuyoshi Satoh

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo, 162, and Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

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Contents

I. Introduction	3303
II. Oxiranyl Anions as Fleeting Intermediates in the Reaction of Epoxides	3303
A. Findings of Oxiranyl Anions	3303
B. Base-Promoted Isomerization of Epoxides to Ketones and Aldehydes	3304
C. Base-Promoted Isomerization of Epoxides with C–H Insertion	3305
D. Olefin Formation with Alkylation	3308
E. Desulfinylation of Sulfinyloxiranes	3311
F. Desilylation of Epoxysilanes and Allene Oxide Formation	3313
III. Generation of Oxiranyl Anions and Trapping with Electrophiles	3315
A. Stabilized Oxiranyl Anions	3315
1. Silicon-Stabilized Oxiranyl Anion	3315
2. Sulfone-Stabilized Oxiranyl Anions	3317
3. Other Stabilized Oxiranyl Anions	3319
B. Nonstabilized Oxiranyl Anions and Destabilized Oxiranyl Anions	3320
IV. Aziridinyl Anions	3321
A. Stabilized Aziridinyl Anions	3321
B. Nonstabilized Aziridinyl Anions	3323
V. Conclusions and Perspective	3324
VI. Acknowledgments	3324
VII. References	3325

I. Introduction

Carbanions are one of the most important, highly reactive intermediates in organic synthesis and innumerable studies on the properties, reactivity, and methods for generation of carbanions have been continued by many chemists.¹ On the other hand, three-membered cyclic compounds containing oxygen and nitrogen in the ring, epoxides and aziridines (Figure 1), are widely recognized as being extremely versatile synthetic intermediates.² Attributable to ring strain, the reactions of epoxides and aziridines with a variety of nucleophiles lead to ring openings under both acidic and basic conditions. Carbon–carbon bond formation, Lewis acid- or base-catalyzed isomerization and rearrangement reactions are of value in organic synthesis. Predictable control of regiochemistry and stereochemistry in nucleophilic ring opening of epoxides and aziridines lends further attraction to their use in organic synthesis. The value of epoxides in organic synthesis has markedly increased especially after disclosure of the asymmetric epoxidation methodology by Sharpless.³

We are able to generate an anion on the ring carbon of epoxides and aziridines. These carbanions are



Tsuyoshi Satoh was born in 1947 in Fukushima, Japan. He studied pharmaceutical sciences at Science University of Tokyo where he received his B.S. degree in 1970. He then moved to Hokkaido University and received his M.S. degree in 1972 under the guidance of Professor Y. Kanaoka. He joined the Science University of Tokyo, Faculty of Pharmaceutical Sciences, as Research Associate in 1972 and was promoted to Lecturer in 1989. He received his Ph.D. from Hokkaido University in the field of total synthesis of natural products in 1979. In 1981, he spent one year at the University of Wisconsin—Madison, where he joined the group of Professor B. M. Trost and studied Pd–TMM complex in organic synthesis. In 1996, he moved to the Department of Chemistry, Science University of Tokyo, as Associate Professor. Dr. Satoh was awarded the 1991 Pharmaceutical Society of Japan (PSJ) Award for Young Scientists. His current research interests focus on organosulfur chemistry, carbanion chemistry, main metal chemistry, asymmetric synthesis, and strained molecules in organic synthesis.

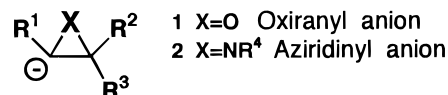


Figure 1.

commonly called oxiranyl anion (1) and aziridinyl anion (2), respectively (Figure 1). Oxiranyl anions (1) and aziridinyl anions (2) were not widely known by chemists and had not been extensively studied. However, recently cumulative studies on the chemistry of oxiranyl anions and aziridinyl anions have appeared and some aspects of these carbanions have been discussed. This review deals comprehensively with the chemistry of oxiranyl anions (1) and aziridinyl anions (2).

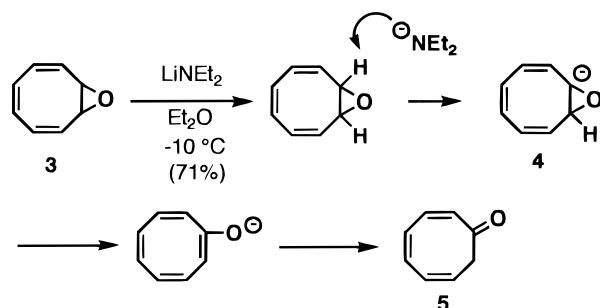
II. Oxiranyl Anions as Fleeting Intermediates in the Reaction of Epoxides

A. Findings of Oxiranyl Anions

In 1951, Cope mentioned for the first time the presence of oxiranyl C-anion as an intermediate in the reaction of cyclooctatetraene oxide with a strong base.⁴ Treatment of cyclooctatetraene oxide (3) with

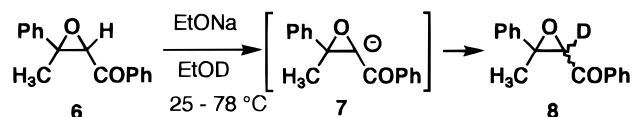
lithium diethylamide in ether gave 1,3,5-cyclooctatrien-7-one (**5**, isolated as a semicarbazone) in 71% yield (Scheme 1).

Scheme 1



As the mechanism of this reaction, Cope proposed the formation of an anion **4** by a base-promoted removal of an α -proton from **3**. The anion **4** rearranged to an enolate, which gave **5** by acidification.⁴ Next, House found that treatment of both *cis*- and *trans*- α -methyl- β -(phenylcarbonyl)acetophenone oxide (**6**) with sodium ethoxide in deuterioethanol led to the formation of a mixture of *cis*- and *trans*-**6**.⁵ Further, one deuterium was incorporated in the epoxide ring to afford **8** (Scheme 2). This report was

Scheme 2

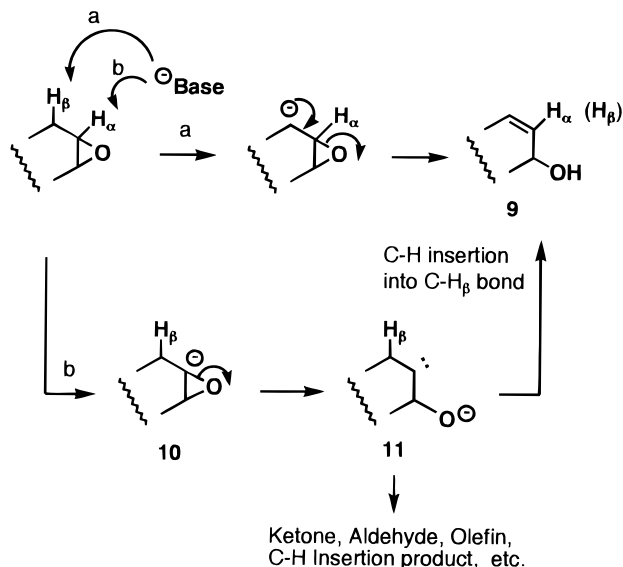


the first to indicate the presence of an oxiranyl anion in the basic treatment of epoxides.

B. Base-Promoted Isomerization of Epoxides to Ketones and Aldehydes

It is well known that the reaction of epoxides with strong bases effects β -hydrogen abstraction to afford allylic alcohols **9** (Scheme 3; path a).⁶ However, this

Scheme 3

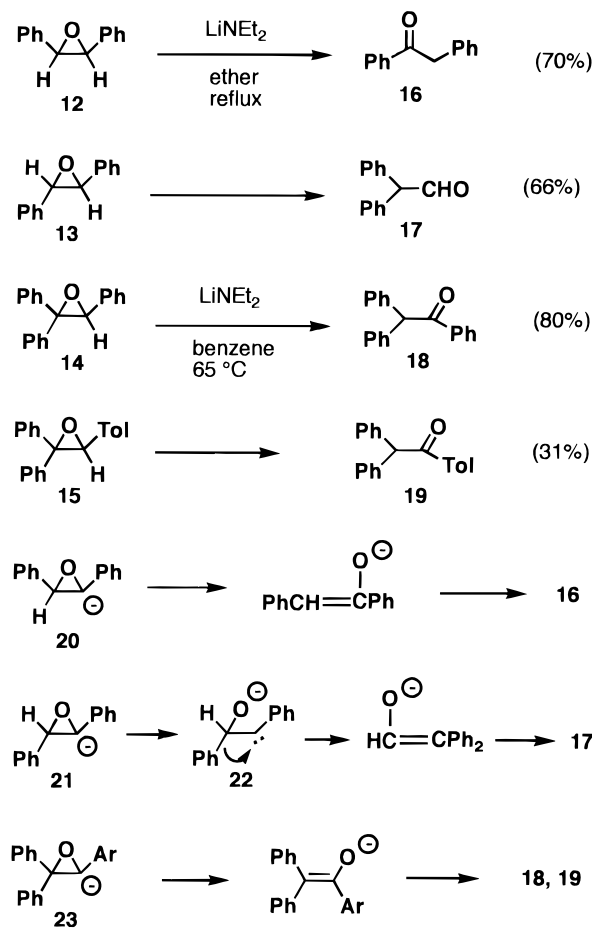


is not always the case. The reaction, in some cases, affects α -hydrogen abstraction to give oxiranyl anion

10 (path b), which rearranges to β -oxido carbenoid **11** through α -elimination. The generated carbenoid shows various interesting reactions such as isomerization to carbonyl compounds, C-H insertion reaction, and backbone rearrangement.⁷

Cope reported that the reaction of *cis*- and *trans*-stilbene oxide (**12** and **13**), triphenylethylene oxide (**14**), 1,1-diphenyl-2-*p*-tolylethylene oxide (**15**) with lithium diethylamide gave ketones and aldehyde **16**–**19** (Scheme 4).⁸ However, under similar conditions,

Scheme 4

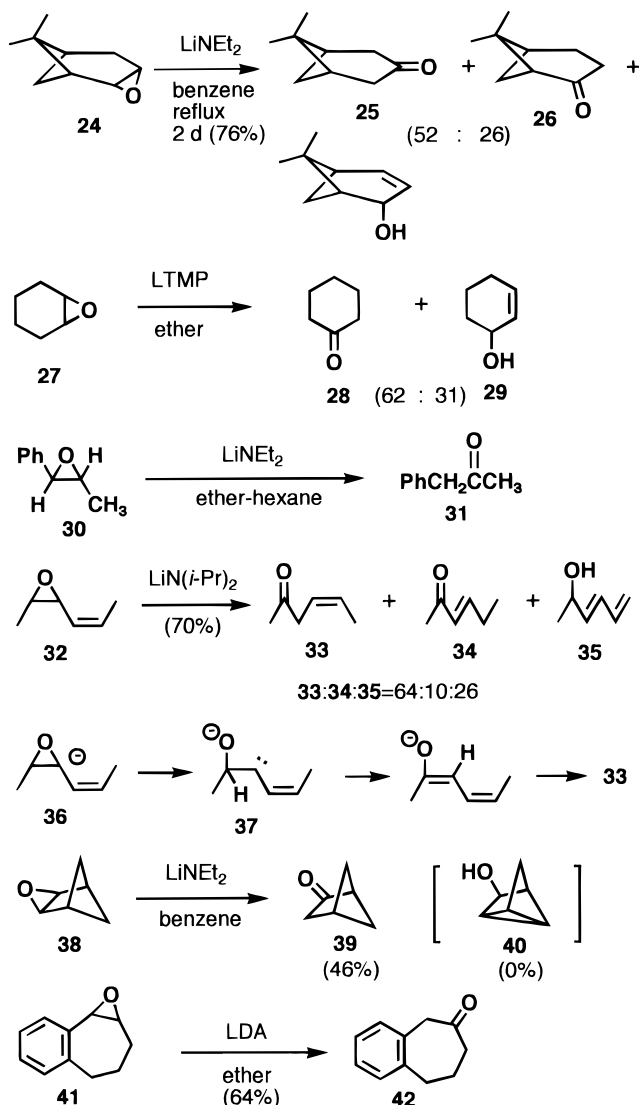


Ar=Ph, Tol

tetraphenylethylene oxide did not react; this result implied that the above reaction proceeded through oxiranyl anions. Formation of ketones **16**, **18**, **19** from **12**, **14**, **15** can be interpreted to arise from the formation of oxiranyl anion **20** followed by rearrangement to enolate. However, formation of aldehyde **17** from **13** was accompanied by a rearrangement of a phenyl group. This reaction is thought to proceed via the rearrangement of oxido carbenoid **22** which was derived from oxiranyl anion **21**.

Other examples of the formation of ketones from epoxides with strong bases are shown in Scheme 5. Apopinene oxide (**24**) gave ketones **25** and **26** with noticeable amount of allylic alcohol in a ratio of 52:26:22 on treatment with lithium diethylamide in refluxing benzene.⁹ Treatment of cyclohexene oxide (**27**) with lithium 2,2,6,6-tetramethylpiperidide (LTMP) led to the formation of cyclohexanone (**28**) and allylic alcohol **29** in a ratio of 62:31. Under the

Scheme 5

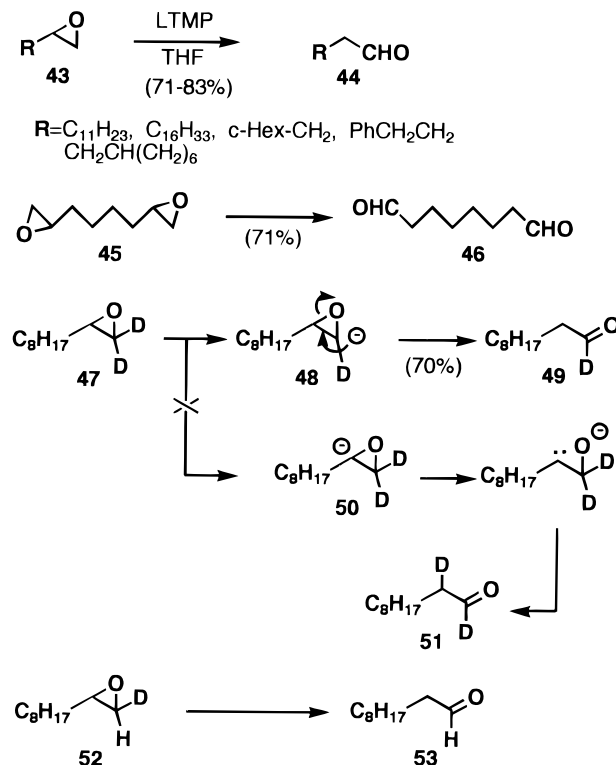


reaction conditions **29** was not isomerized to **28**; the cyclohexanone is a primary product derived from oxiranyl anion.^{10a} A more detailed study for the mechanisms of the base-induced isomerization of cyclopentene and cyclohexene oxide was recently reported by Morgan.^{10b} Treatment of β -methylstyrene oxide (**30**) with lithium diethylamide afforded benzyl methyl ketone (**31**).¹¹

cis,cis-Diene monoepoxide **32** produced ketones **33** and **34** on treatment with lithium diisopropylamide (LDA).¹² Ketone **34** was derived from **33** through double-bond migration under the basic conditions. Ketone **33** was produced via the oxido carbenoid rearrangement of **37**. Treatment of 2,3-epoxybicyclo[2.1.1]hexane (**38**) with lithium diethylamide in benzene afforded ketone **39**. The expected C-H insertion (*vide infra*) product **40** was not observed.¹³ Reaction of benzocycloheptene oxide (**41**) with LDA in ether at room temperature gave only β -ketone **42**.¹⁴

Recently, the first example of the formation of aldehydes from the reaction of 1,2-epoxyalkanes with a base was reported by Yamamoto (Scheme 6).¹⁵ Treatment of 1,2-epoxyalkanes **43** with LTMP in THF at room temperature led to the formation of aldehydes **44** in good yields. Diepoxide **45** also smoothly produced dialdehyde **46**. The mechanism of this reaction

Scheme 6

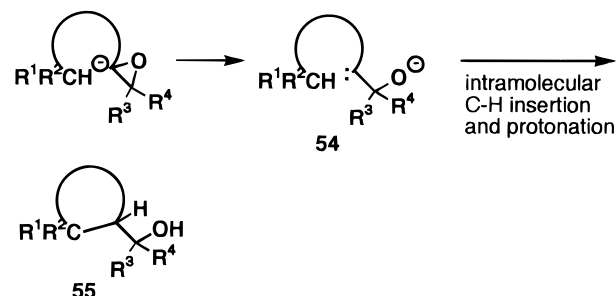


was investigated using deuterated epoxides **47** and **52**. Thus, treatment of **47** with LTMP afforded monodeuterated aldehyde **49**. From this result, it is apparent that the reaction proceeded through oxiranyl carbenoid **48**. Further, because this reaction did not give **51**, oxiranyl anion **50** was not generated. As the reaction of **52** with LTMP afforded **53**, *trans*-proton at the epoxide ring was found to be selectively eliminated by LTMP. This selectivity is quite interesting.

C. Base-Promoted Isomerization of Epoxides with C-H Insertion

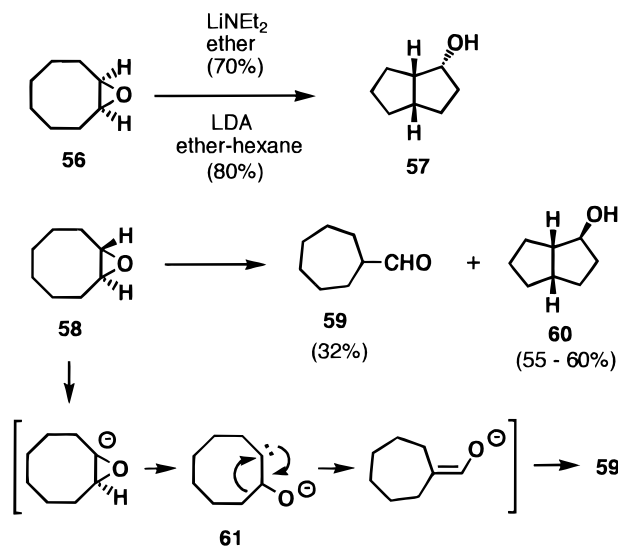
Carbenes and carbenoids react with C-H bond (C-H insertion reaction) to afford carbon-carbon bonds.⁷ When this reaction proceeds in an intramolecular fashion, a new ring will be produced. Oxiranyl anions are very unstable and in the produced β -oxido carbenoid **54**, in some cases, C-H insertion reaction takes place to afford cyclic alcohol **55** (Scheme 7).

Scheme 7



Cope obtained bicyclic[3.3.0]octan-2-ol (**57**) from *cis*-cyclooctene oxide (**56**) with lithium diethylamide in good yield.¹⁶ This report is the first example of the transannular C-H insertion reaction from cyclic epoxide by basic treatment (Scheme 8). Interest-

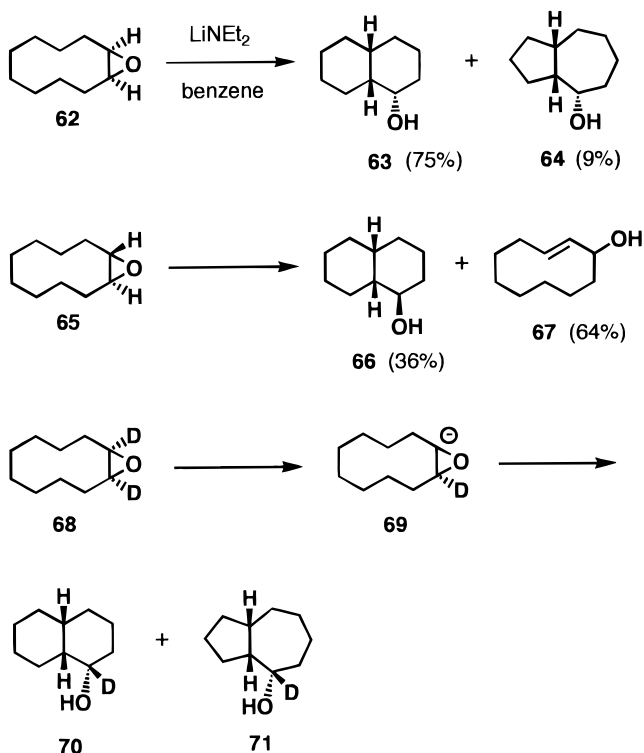
Scheme 8



ingly, the reaction of *trans*-cyclooctene oxide (**58**) afforded isomer **60**. These results implied that the intermediate in these reactions was not free carbene but carbenoid. The reaction of **58** also gave ring-contracted aldehyde **59** in 32% yield. This aldehyde **59** was derived from **58** via the rearrangement of β -oxido carbenoid **61**. Formation of **57** from epoxide **56** was reported to give better yield by using LDA in ether-hexane.¹⁷

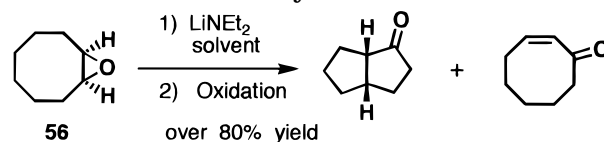
Reaction of *cis*-cyclodecene oxide (**62**) with lithium diethylamide in benzene afforded two bicyclic alcohols **63** and **64** in good yields. *trans*-Oxide **65** afforded bicyclic alcohol **66**; however, the main product was allylic alcohol **67** (Scheme 9).¹⁸ This reaction

Scheme 9



proceeded through an oxiranyl anion, which was confirmed by an experiment using deuterated epoxide **68**.¹⁹ The reaction of **68** gave bicyclic alcohols **70** and

Table 1. Solvents and Temperature Effect of the LiNEt_2 Isomerization of Cyclooctene Oxide



Solvents and temperature	Ratio of products	
	Bicyclic ketone	Enone
ether / heat / 48 h	65	35
ether-hexane / heat / 48 h (about 1:1)	8	92
THF / heat / 48 h	7	93
THF / HMPA (1 eq) / heat / 48 h	9	91
ether / HMPA / room temp. / 6 d	4	96

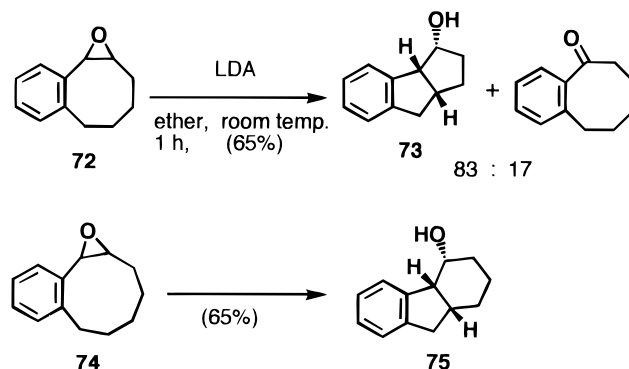
71. These alcohols had one deuterium on the carbon bearing a hydroxyl group. This result implied that the intermediate of this reaction was oxiranyl anion **69**.

Boeckman investigated the solvent effect and temperature effect of the reaction of cyclooctene oxide with lithium diethylamide (Table 1).²⁰ As shown in the table, little or no solvent dependence was observed; however, the reaction was found to be extremely temperature dependent. Moreover, increasing polarity of the medium tends to give allylic alcohol.

Table 2 shows the ring size of the cyclic epoxides and the ratio of the products.²⁰ The table shows that the transannular cyclization is favorable between 8-10-membered cyclic epoxides.

Reaction of benzocycloalkene oxide (**72**) with LDA in ether at room temperature gave bicyclic alcohol **73** as the main product (Scheme 10).¹⁴ Similarly,

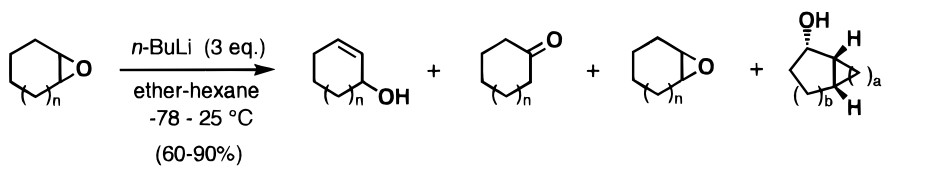
Scheme 10



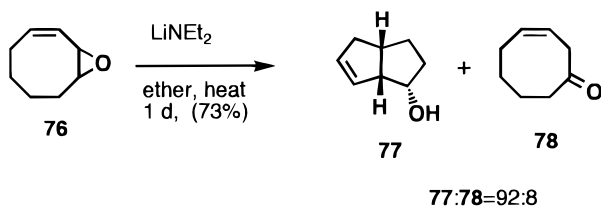
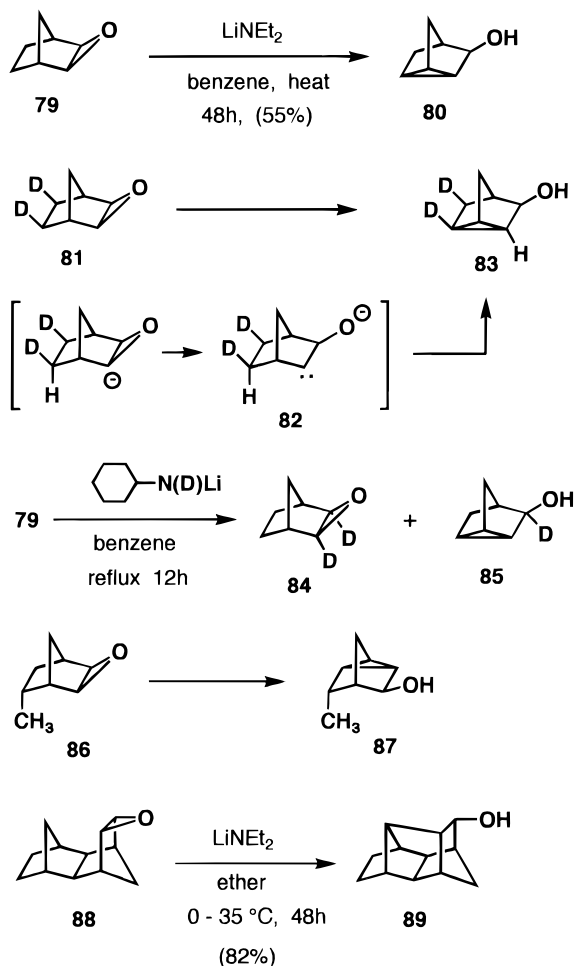
oxide **74** afforded bicyclic alcohol **75** in good yield. As the hydrogen on the oxirane ring of **72** and **74** is more acidic than nonbenzo compounds, the reaction was completed within 1 h.

Treatment of 3,4-epoxycyclooctene (**76**) with lithium diethylamide led to the formation of bicyclic alcohol **77** and 3-cyclooctenone **78** (Scheme 11).²¹

Basic treatment of fixed bicyclic epoxides led to transannular cyclization. Heating of norbornene oxide (**79**) with lithium diethylamide in benzene gave nortricyclanol (**80**, Scheme 12).²² The carbenoid

Table 2. Ring Size and Products Distribution


n	Alcohol	Ketone	Epoxide	Bicyclic Alcohol
n=1	29	56	15	0
n=2	0	84	3	13 (a=1, b=2)
n=3 (cis)	0	0	1	99 (a=3, b=1)
n=5 (cis)	1	0	0.5	97.5 (a=4, b=2)
n=7	80	10	10	0

Scheme 11**Scheme 12**

mechanism of this reaction was confirmed by using deuterium-labeled epoxide **81**.²³ When epoxide **81** was treated under the same conditions, nortricyclanol **83** was obtained and it was found that all the deuterium label was retained. This result was expected that the intermediate of this reaction was carbenoid **82** and C–H insertion reaction occurred into the endo carbon–hydrogen bond.

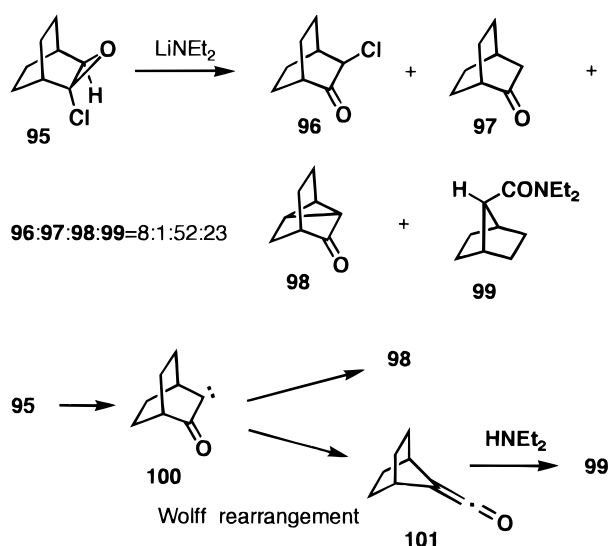
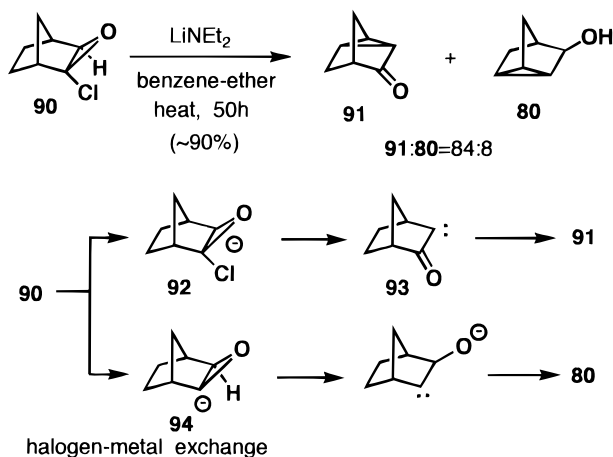
Direct evidence for metalation at the epoxide ring was confirmed as follows. Upon heating with deuterated lithium cyclohexylamide, oxide **79** afforded epoxide **84** and tricyclic alcohol **85**. The recovered epoxide **84** had exchanged 84% of its epoxy protons. Moreover, 69% deuterium was present at the carbinol position of the alcohol **85**. Epoxide **86** gave only tricyclic alcohol **87**.²³ Treatment of **88** with lithium diethylamide afforded pentacyclo[6.4.0^{2.10}.0^{3.7}.0^{5.9}]-dodecane system **89** in good yield.²⁴

McDonald obtained tricyclic ketone **91** and tricyclic alcohol **80** from α -chloro epoxide **90** with lithium diethylamide.²⁵ Tricyclic ketone **91** was expected to be produced from carbenoid **93** which was derived from oxiranyl anion **92** (Scheme 13). Alcohol **80** was formed via oxiranyl anion **94** which was derived from **90** by halogen–lithium exchange.

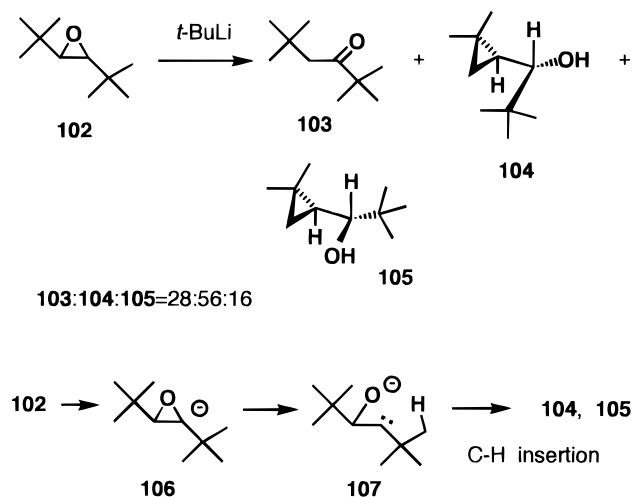
A similar reaction of α -chloro epoxide **95** gave tricyclic ketone **98** and amide **99** as main products. These two carbonyl compounds were thought to be derived from **95** via keto carbenoid **100**. Wolff ring contraction of **100** gives amide **99** via ketene **101**.

Reaction of *trans*-di-*tert*-butylethylene oxide (**102**) with *tert*-butyllithium (*t*-BuLi) in hydrocarbon solution gave ketone **103** and two cyclopropylcarbinols **104** and **105** (Scheme 14).²⁶ The formation of **104** and **105** is rationalized by the sequence of metalation (to give **106**), α -elimination (to give **107**), and carbenoid insertion into a C–H bond of the adjacent *tert*-butyl substituent.

Scheme 13



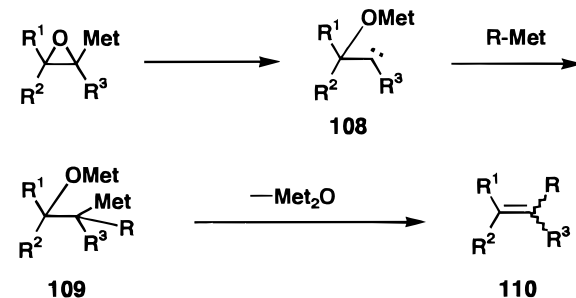
Scheme 14



D. Olefin Formation with Alkylation

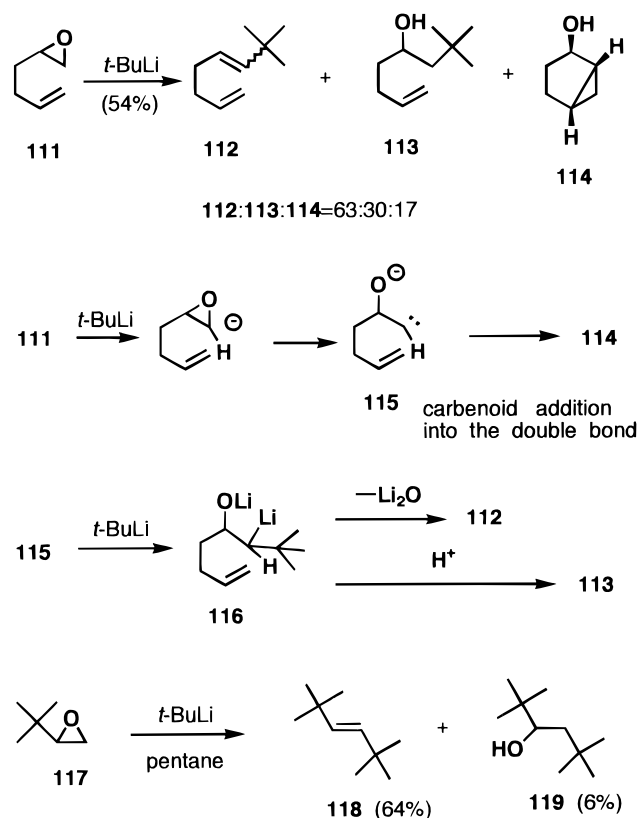
α -Alkoxy-carbenoid **108**, which is derived by the α -elimination of the oxiranyl anion, reacts with organometallic compounds to give dianion **109**. Metal oxide (Met_2O) is then eliminated to afford alkylated olefin **110** (Scheme 15).

Scheme 15



Crandall obtained products **112**–**114** from 5,6-epoxy-1-hexene (**111**) with $t\text{-BuLi}$ in 54% yield (Scheme 16).²⁶ The mechanism of this reaction was

Scheme 16



proposed as follows. The reaction of **111** with $t\text{-BuLi}$ results in the formation of carbenoid **115** via an oxiranyl lithium. Bicyclic alcohol **114** is obtained by carbenoid addition into the double bond. The carbenoid **115** reacts with $t\text{-BuLi}$ to generate dianion **116**. Protonation of **116** produces alcohol **113**. Elimination of lithium oxide from **116** affords alkylated olefin **112**. This is the first report of the synthesis of alkylated olefins from epoxides with alkylmetal.

Treatment of *tert*-butylethylene oxide (**117**) with $t\text{-BuLi}$ in pentane led to the formation of *trans*-di-*tert*-butylethylene (**118**) and alcohol **119**.²⁷ The mechanism of this reaction was thought to be similar to that described above.

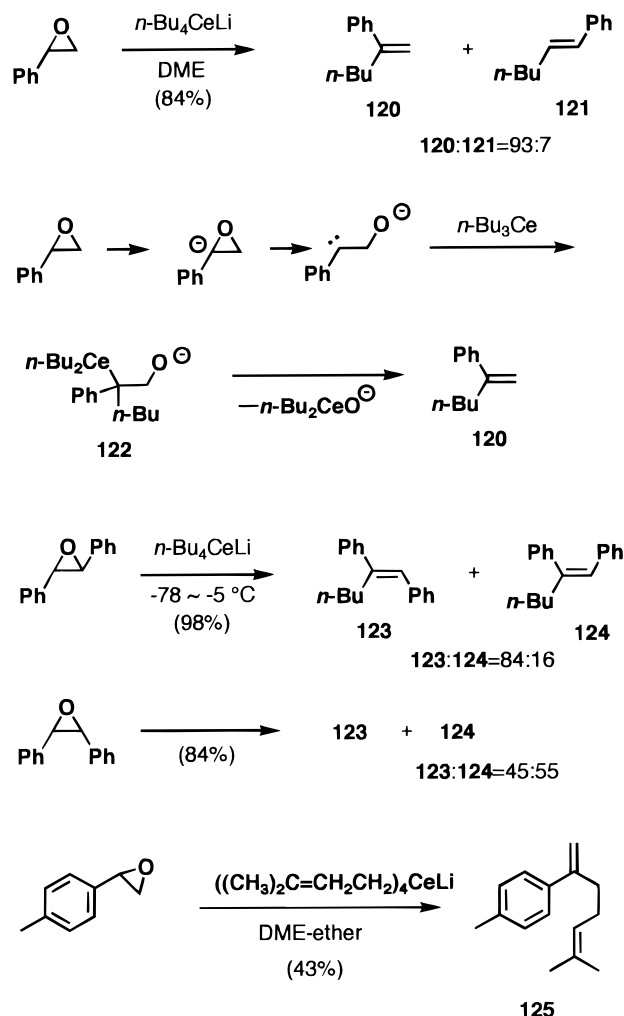
Recently, Mioskowski reported the reaction of various epoxides with alkyllithiums giving alkylated olefins in variable yield (Table 3).²⁸

Table 3. Olefin Formation with Alkylation from Epoxides

Entry	Epoxide	RLi	Conditions	Olefin (Yield / %)
		RLi	THF	
1		<i>s</i> -BuLi	-70 °C ~ rt 90 min	 (76)
2		<i>s</i> -BuLi	-70 °C ~ rt 90 min	 (65)
3		<i>t</i> -BuLi	-70 °C ~ rt 90 min	 (98)
4		<i>t</i> -BuLi	-70 °C ~ rt overnight	 (95)
5		<i>t</i> -BuLi	-70 °C ~ rt overnight	 (82)
6		MeLi	-70 °C ~ rt overnight	 (32) (16)
7		<i>s</i> -BuLi	-70 °C 20 min	 (8) (21)
8		<i>t</i> -BuLi	-70 °C ~ rt over night	 (56)
9		<i>s</i> -BuLi	-70 ~ -10 °C 1 h	 (15)
				R=(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ OCH ₃

In the case of mono-substituted epoxides, the metalation occurs at the less hindered side (entries 3, 4, 6). However, in the case of the phenyl-substituted epoxide, both sides were metalated, mainly the benzyl position (entry 7). The hydrogen at *trans*-position was stereoselectively eliminated by *t*-BuLi (entry 4). *trans*-Olefins were obtained when a bulky organolithium reagent was used (entries 3, 4; compare with the reaction with methyl lithium, which gave a mixture of *trans*- and *cis*-olefins; entry 6). In the case of 1,2-disubstituted epoxides, high stereospecificity was obtained (entries 1, 2). This reaction was possible with cyclic epoxide (entry 8). Even trisubstituted epoxide gave tetrasubstituted olefin, though the yield was low (entry 9).

Fujisawa reported a similar conversion of epoxides to substituted olefins with lithium tetraalkylcerate (Scheme 17).²⁹ Treatment of styrene oxide with lithium tetrabutylcerate in DME gave olefins **120** and **121** in good yield. The mechanism of this reaction was proposed as follows. The carbenoid inserts into the carbon–cerium bond to give **122**. β -Elimination of cerium oxide then occurs to afford substituted terminal olefin **120**.

Scheme 17

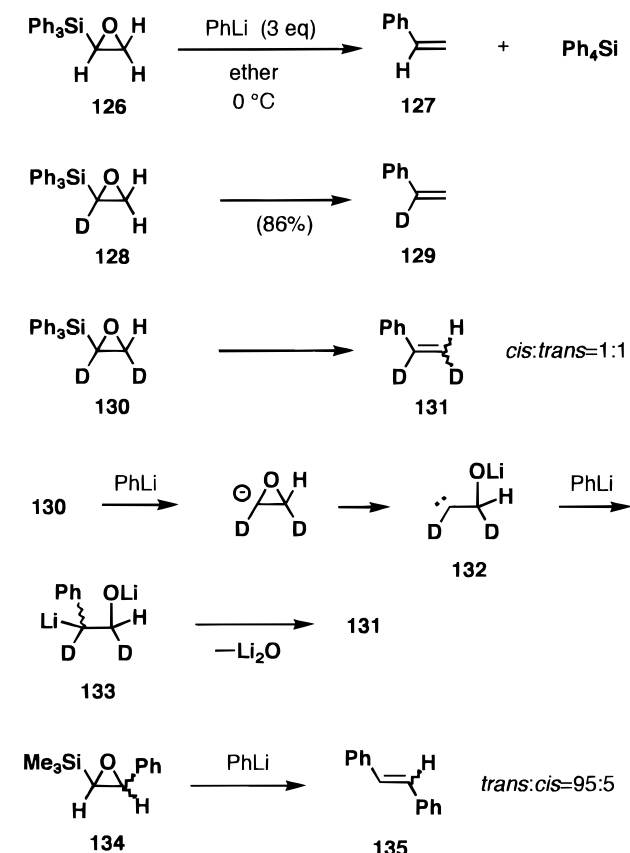
Lithium tetraalkylcerates reacted well with epoxides when the alkyl group was methyl, *n*-butyl, or *tert*-butyl. The reaction of *trans*-stilbene oxide gave mainly (*E*)-olefin **123**. *cis*-Stilbene oxide gave mainly (*Z*)-olefin **124**; however, the stereoselectivity was low. By this method dehydro- α -curcumene (**125**) was synthesized in moderate yield.

Some reports on the formation of alkylated olefins from epoxides and epoxy stannanes with alkylmetals have been published. Eisch obtained styrene **127** and tetraphenylsilane on treatment of epoxy silane **126** with phenyllithium in ether (Scheme 18).³⁰ The reaction of α -deuterated epoxide **128** gave deuterium-labeled styrene **129**. The reaction of dideuterated epoxide **130** afforded α,β -dideuteriostyrene (**131**) and it was found that **131** was a mixture of *cis*- and *trans*-isomers.

Obviously this reaction proceeded via an oxiranyl anion which was derived from the epoxy silanes by silicon–lithium exchange. The produced oxiranyl anion gave carbenoid **132** by α -elimination, and then **132** reacted with phenyllithium to afford dianion **133**. The lack of stereoselectivity in the reaction of **130** with phenyllithium can be explained if the reaction of **132** with phenyllithium is nonstereoselective. However, in a similar manner both *cis*-**134** and *trans*-**134** selectively gave *trans*-stilbene (**135**).

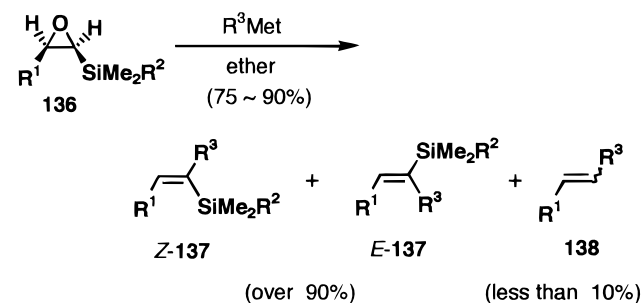
Fujisawa reported the reaction of *cis*-epoxy silane **136** with various alkylolithiums or organolanthana-

Scheme 18



noids in ether giving vinylsilanes **137** in good yield (Scheme 19).³¹ In this reaction alkene **138** was

Scheme 19

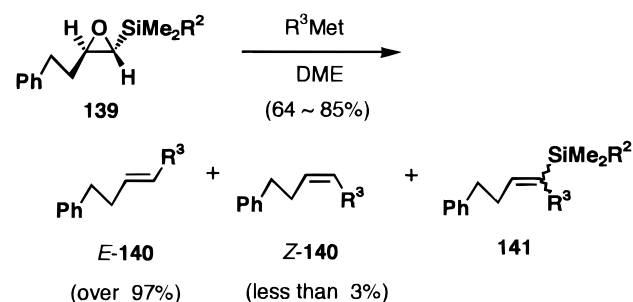


R¹=PhCH₂CH₂, R²=Me

R¹=PhCH₂CH₂, R²=Ph

R¹=*n*-Bu, R²=Me

R³Met: *n*-BuLi, *t*-BuLi, *n*-C₅H₁₁Li, *n*-BuCeCl₂, *n*-BuLaCl₂,
n-BuSmCl₂, *n*-C₅H₁₁LaCl₂, *t*-BuLaCl₂



R³Met: *n*-BuLi, *n*-BuCeCl₂, *n*-BuLaCl₂, PhCeCl₂, PhLi

Table 4. Vinylsilanes from *cis*-Epoxy Silane

Entry	R ¹	R	R ² Li	Vinylsilane	
				Yield / %	<i>E</i> / <i>Z</i>
1	<i>n</i> -Bu	Me	<i>t</i> -BuLi	93	16 / 84
2	Me	Et	<i>n</i> -BuLi	81	8 / 92
3	Me	Et	<i>t</i> -BuLi	97	5 / 95
4	<i>n</i> -Bu	Et	<i>n</i> -BuLi	80	24 / 76
5	<i>n</i> -Bu	Et	<i>t</i> -BuLi	100	12 / 88
6	<i>i</i> -Pr	Et	<i>n</i> -BuLi	79	62 / 38
7	<i>i</i> -Pr	Et	<i>t</i> -BuLi	57	95 / 5
8	Me	<i>i</i> -Pr	MeLi	85	95 / 5
9	Me	<i>i</i> -Pr	<i>n</i> -BuLi	82	99 / 1
10	Me	<i>i</i> -Pr	TMSCH ₂ Li	90	96 / 4
11	Me	<i>i</i> -Pr	<i>t</i> -BuLi	89	99 / 1

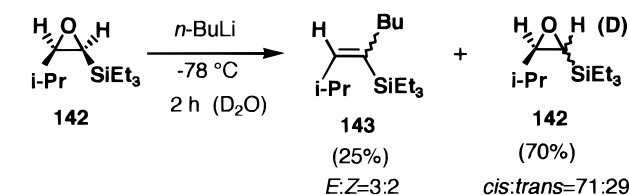
produced as a byproduct; however, the yield of **138** was usually less than 10%. Moreover, stereoselectivity of this reaction was shown to be very high and (*Z*)-vinylsilane (*Z*-**137**) was obtained in over 90% selectivity.

Interestingly, when the reaction of *trans*-epoxy silane **139** with alkylmetals was carried out in DME, olefins **140** were produced as main products; yield of vinylsilane **141** was less than 5%. Stereoselectivity of this reaction was very high, giving (*E*)-olefin. The large difference in these reactions is explained as follows. When the reaction is carried out in ether, proton abstraction takes place to afford vinylsilanes. On the other hand, silicon–lithium exchange takes place when **139** was reacted with alkylmetals in DME.

Soderquist synthesized various 1,2-dialkylvinylsilanes from *cis*- α -epoxy silanes with alkyl lithium (Table 4).³² The yields are generally very high. The stereochemistry of the produced vinylsilanes is interesting. Stereochemistry of the vinylsilanes changes with the size of either SiR₃ or R¹. In the case where R¹ is the primary alkyl and SiR₃ is less bulky, (*Z*)-vinylsilanes are predominantly obtained. The epoxy silanes having a bulky silyl group afford (*E*)-vinylsilanes with quite high stereoselectivity.

Reaction of *cis*-epoxy silane **142** with *n*-butyllithium (*n*-BuLi) at -78°C for 2 h gave vinylsilane **143**, and starting material **142** was recovered in 70% yield (Scheme 20). The recovered **142** was found to

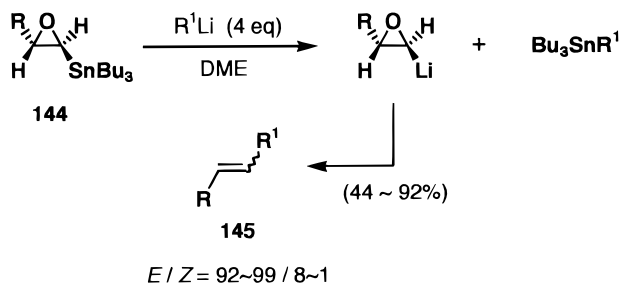
Scheme 20



be a mixture of *cis/trans*-isomers, which indicated that the intermediate, oxiranyllithium, was partially inverted. Moreover, quenching this reaction with deuterium oxide gave α -deuterated epoxide.³²

Treatment of *trans*- α -epoxy stannanes **144** with excess alkyl lithium led to tin–lithium exchange to afford oxiranyllithium. This gave (*E*)-olefin **145** via a carbenoid intermediate in high stereoselectivity (Scheme 21).³³

Scheme 21

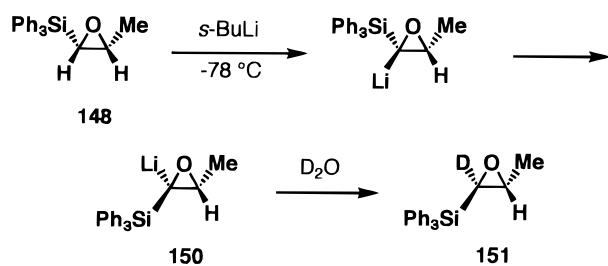


R = *n*-C₅H₁₁, *i*-Pr, SiMe₃
R¹Li = *n*-BuLi, *t*-BuLi, TMSCH₂Li

Utimoto reported that the reaction of epoxy silanes **146** with *sec*-butyllithium (*sec*-BuLi) followed by alkylaluminum gave substituted (triphenylsilyl)alkene **147** in good yield (Table 5).³⁴ The reaction with trialkylaluminum generally gave **147** in good to high yields. A heteroatom as well as a butylthio group can be introduced by the use of R₂AlX (X = Cl, I, *n*-BuS). Alkenyl and alkynyl groups are transferred in preference to an alkyl group. Both *cis*- and *trans*-1-methyl-2-(triphenylsilyl)oxiranes **148** give the same (*E*)-2-(triphenylsilyl)-2-butene (**149**) in high stereoselectivity.

In this reaction, configurational inversion was observed in the case of **148** (Scheme 22). After the

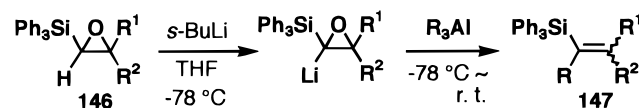
Scheme 22



reaction of *cis*-epoxide **148** with *s*-BuLi at -78 °C, the reaction was quenched with deuterium oxide to afford deuterated *trans*-epoxide **151**. This result showed that in the reaction oxiranyllithium intermediate **150** was generated from *cis*-**148** with inversion of the configuration. The configurational instability of the oxiranyllithium intermediate is the reason why both *cis*- and *trans*-**148** afforded the same olefin **149**.

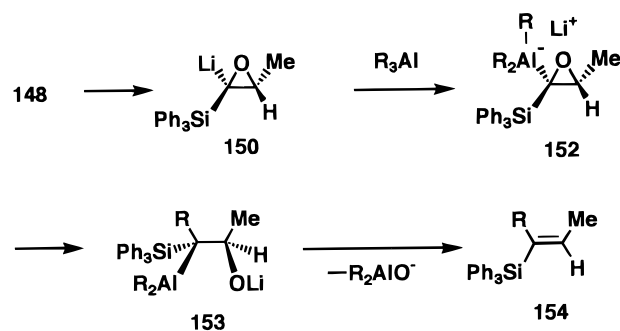
The mechanism of this reaction was proposed to be as follows (Scheme 23). The reaction of oxiranyllithium **150** with alkylaluminum produces aluminum ate complex **152**. 1,2-Migration of the alkyl group from aluminum with cleavage of the oxiranyl ring affords **153**. *Syn*-Elimination of aluminum oxide

Table 5. Triphenylsilyl-Substituted Alkenes from Epoxy Silane



Epoxy 146	R ₃ Al	Alkene 147 (Yield / %)
Ph ₃ Si-O	Me ₃ Al	Ph ₃ Si-C=C-R R= Me (86)
	Et ₃ Al	Ph ₃ Si-C=C-R R= Et (83)
	Et ₂ AlCl	R= Cl (78), R= Et (8)
	Et ₂ AlI	R= I (77), R= Et (3)
	<i>i</i> -Bu ₂ AlCH=CH(CH ₂) ₃ CH ₃	R= CH=CH(CH ₂) ₃ CH ₃ (80)
<i>i</i> -Bu ₂ Al≡SiMe ₃	R= ≡SiMe ₃ (75) R= <i>i</i> -Bu (9)	
Ph ₃ Si-O Me	Me ₂ Al(<i>n</i> -Bu)	R= <i>n</i> -BuS (52), R= Me (17)
	Et ₂ Zn	R= Et (87)
Ph ₃ Si-O Me <i>cis</i> - 148	Me ₃ Al	Ph ₃ Si-C=C(H)Me R= Me (92)
	Et ₂ AlCl	R=Cl (60), R= Et (23)
Ph ₃ Si-O Me <i>trans</i> - 148	Me ₃ Al	Ph ₃ Si-C=C(H)Me R= Me (93)
	Et ₃ Al	R= Et (92)
Ph ₃ Si-O Me Me	Me ₃ Al	Ph ₃ Si-C=C(Me)Me R= Me (83)

Scheme 23



from **153** gives alkylated (triphenylsilyl)alkene **154** stereoselectively.³⁴

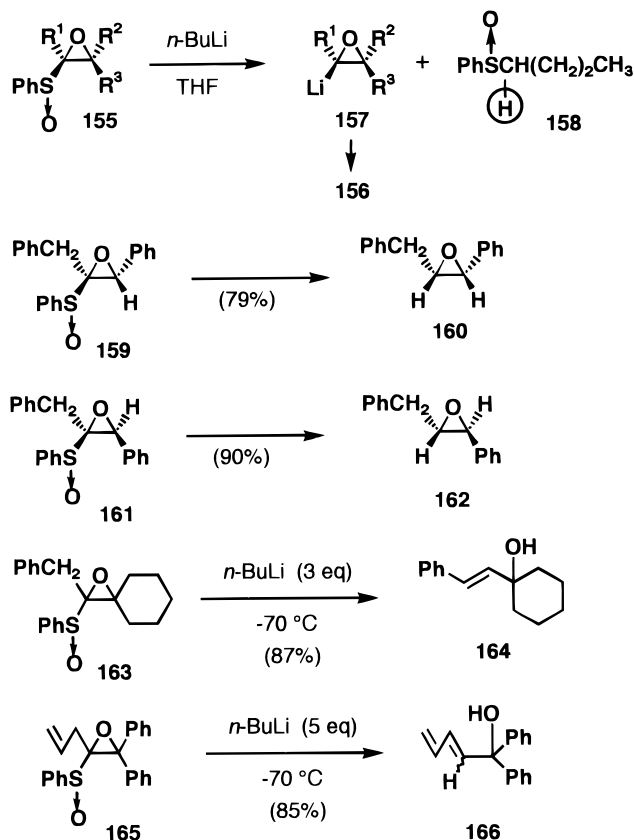
E. Desulfonylation of Sulfinyloxiranes

Treatment of sulfinyloxirane **155** with *n*-BuLi in THF at low temperature led to the formation of desulfonylated epoxide **156** in good yield (Table 6).³⁵

The mechanism of this reaction is as follows (Scheme 24). The reaction of sulfinyloxirane **155** with *n*-BuLi effects the ligand exchange reaction of sulfoxide³⁶ to give oxiranyllithium **157** and butyl phenyl sulfoxide **158**. Oxiranyllithium **157** quickly picks up the acidic proton of sulfoxide **158** to generate

Table 6. Desulfinylation of Sulfinyloxirane with *n*-Butyllithium

Sulfinyloxirane 155			Temp. °C	Epoxide 156 Yield / %
R ¹	R ²	R ³		
CH ₃ (CH ₂) ₅	—(CH ₂) ₅ —		-70	89
PhCH ₂	CH ₃	CH ₃	-100	71
	CH ₃ (CH ₂) ₅	H	-70	97
PhCH ₂	Ph	H	-100	90
	—(CH ₂) ₅ —		-100	78
CH ₂ =CHCH ₂	Ph	Ph	-100	85

Scheme 24

epoxide **156**.³⁷ Isomeric sulfinyloxiranes **159** and **161** gave epoxides **160** and **162**, respectively, on treatment with *n*-BuLi at -100 °C. This result implies that the configurational stability of the oxiranyl-lithium **157** is high under the reaction conditions. Sulfinyloxiranes having benzyl and allyl group **163** and **165** afforded desulfinylated allylic alcohols **164** and **166**, respectively, with excess *n*-BuLi at -70 °C.³⁷

This procedure was extended to a method for asymmetric synthesis of optically active epoxides

Table 7. Synthesis of (*S*)-Epoxides **178 from **169** and Symmetrical Ketones**

Ketone	176 Yield / %	177 Yield / %	178 Yield / %	[α] _D
R ¹				
CH ₃	100	98	73	-13.7
Ph	— ^{a)}	99	89	-28.6
—(CH ₂) ₅ —	93	95	85	-14.0
—(CH ₂) ₆ —	84	86	61 (93) ^{b)}	-13.7

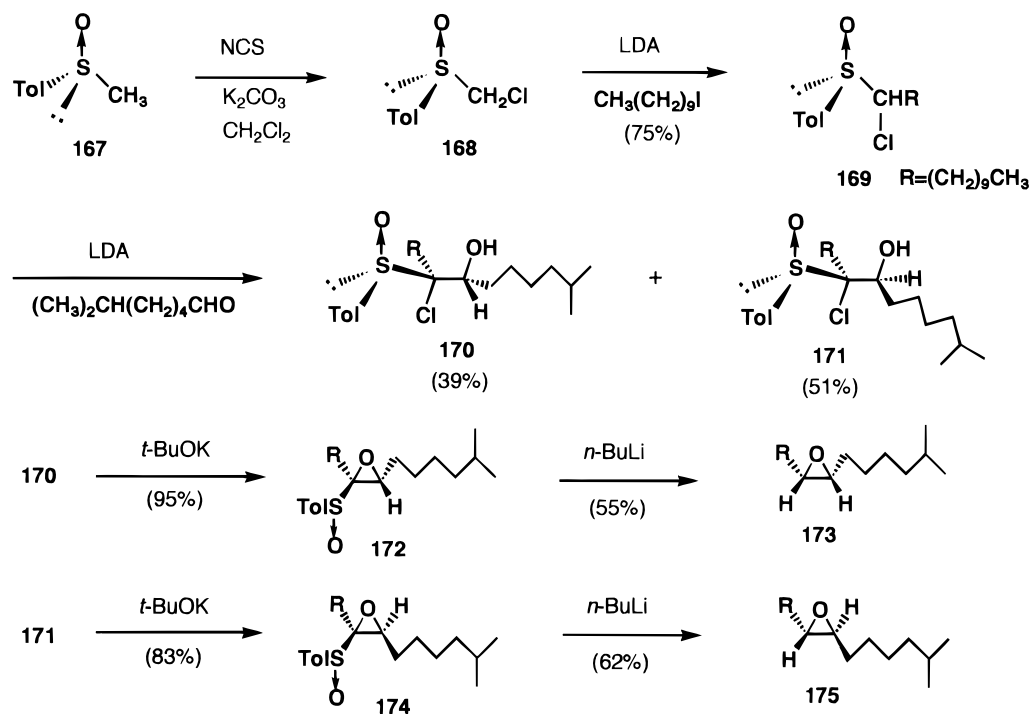
a) Not isolated. b) Conversion yield.

starting from optically active sulfoxide (Scheme 25).^{38–40} Chlorination of optically pure methyl *p*-tolyl sulfoxide (**167**) with *N*-chlorosuccinimide in the presence of potassium carbonate in dichloromethane afforded optically active (–)-chloromethyl *p*-tolyl sulfoxide (**168**) in good yield with inversion of the sulfur chiral center. Generation of the carbanion of **168** with LDA followed by alkylation with iododecane gave alkylated sulfoxide **169** as a mixture of two diastereomers.

Addition of the carbanion of **169** with 6-methylheptanal gave two adducts **170** and **171** in high yield. In this reaction very high 1,2-asymmetric induction from the sulfur chiral center was observed. These chloro alcohols **170** and **171** were separated and treated with potassium *tert*-butoxide to give sulfinyloxiranes **172** and **174**. The stereospecific desulfinylation of **172** was carried out with *n*-BuLi in THF at -100 °C to give optically pure (+)-disparlure (**173**), the sex attractant of the female gypsy moth in moderate yield. Under similar conditions **174** gave (–)-(7*S*,8*S*)-*trans*-disparlure (**175**).^{38, 40}

This method for the asymmetric synthesis of epoxides is most effective when symmetrical ketones are used as carbonyl compounds (Table 7).^{39,40} Optically active sulfoxide **169** was reacted with symmetrical ketone under similar conditions as described above to give chloro alcohol **176** in high yield. Basic treatment of **176** afforded sulfinyloxirane **177** in quantitative yield. The desulfinylation was carried out with *n*-BuLi in THF at -100 °C to afford optically pure (*S*)-(–)-epoxide **178** in good yield. This procedure is very useful for the preparation of optically pure epoxides from carbonyl compounds with carbon–carbon bond formation.

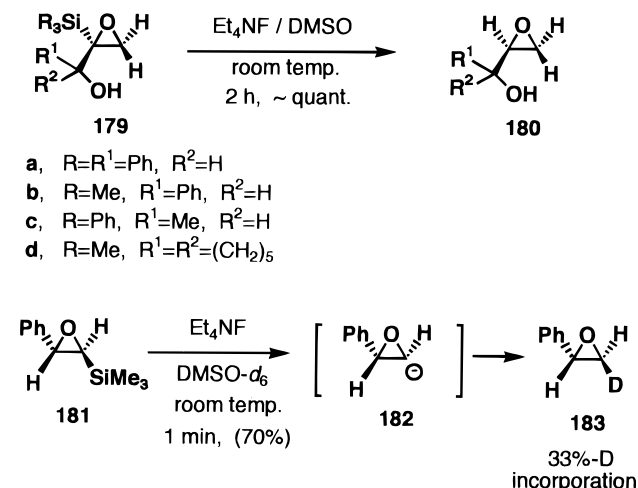
Scheme 25



F. Desilylation of Epoxy silanes and Allene Oxide Formation

The cleavage of the silicon-carbon bond by a fluoride ion is well known.⁴¹ Treatment of epoxy silanes having a β -hydroxy group **179** with tetraethylammonium fluoride in DMSO led to the formation of epoxide **180** in quantitative yield (Scheme 26).⁴²

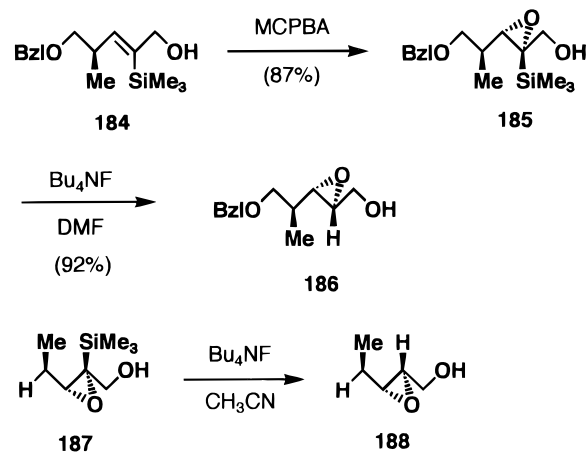
Scheme 26



The replacement of the silyl group by hydrogen can be achieved even without assistance of the β -hydroxy group. Treatment of **181** with tetraethylammonium fluoride in deuterated DMSO gave stereospecifically deuterated epoxide **183**. This result indicates that the reaction proceeded via oxiranyl anion **182**. Moreover, it shows that the replacement of the silyl group by hydrogen occurred with retention of the configuration at the silylated carbon.

Kishi achieved a stereoselective epoxidation of allylic alcohols by the use of this stereospecific desilylation (Scheme 27).⁴³ Epoxidation of allylic

Scheme 27

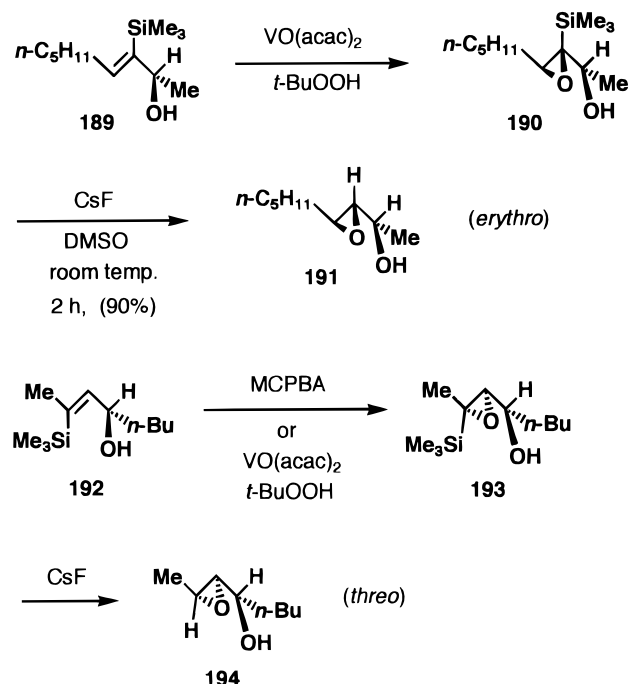


alcohol **184** with *m*-chloroperbenzoic acid (MCPBA) afforded epoxy silane **185** in high stereoselectivity. Stereospecific desilylation was conducted with tetrabutylammonium fluoride in DMF to give **186** in high yield. The desilylation of **187** was achieved in acetonitrile to afford **188**.

A similar study was reported by Nozaki (Scheme 28).⁴⁴ Highly stereoselective epoxidation of the silylated allylic alcohol **189** and **192** was carried out with *tert*-butyl hydroperoxide or MCPBA to give **190** and **193**, respectively. The desilylation of **190** and **193** was conducted with cesium fluoride in DMSO to afford *erythro*-allylic alcohol **191** and *threo*-allylic alcohol **194**, respectively, in high yield.

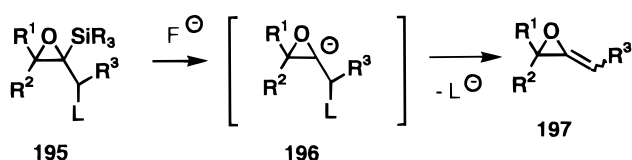
Allene oxide **197** is a highly strained and highly reactive compound.⁴⁵ As one approach to the

Scheme 28



preparation of allene oxides, Chan reported a method from epoxy silane **195** as shown in Scheme 29. This

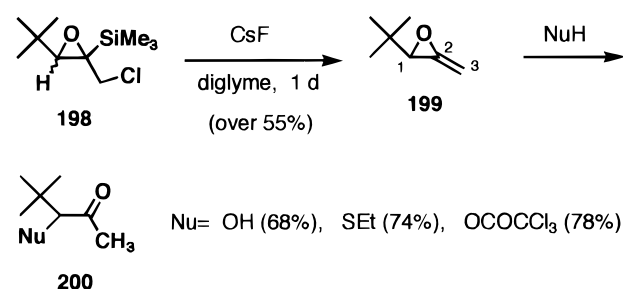
Scheme 29



reaction is thought to proceed via oxiranyl anion **196** as a fleeting intermediate.

Upon treatment of epoxy silane **198** with cesium fluoride in diglyme at room temperature, allene oxide **199** was isolated in moderate yield (Scheme 30).^{46,47}

Scheme 30

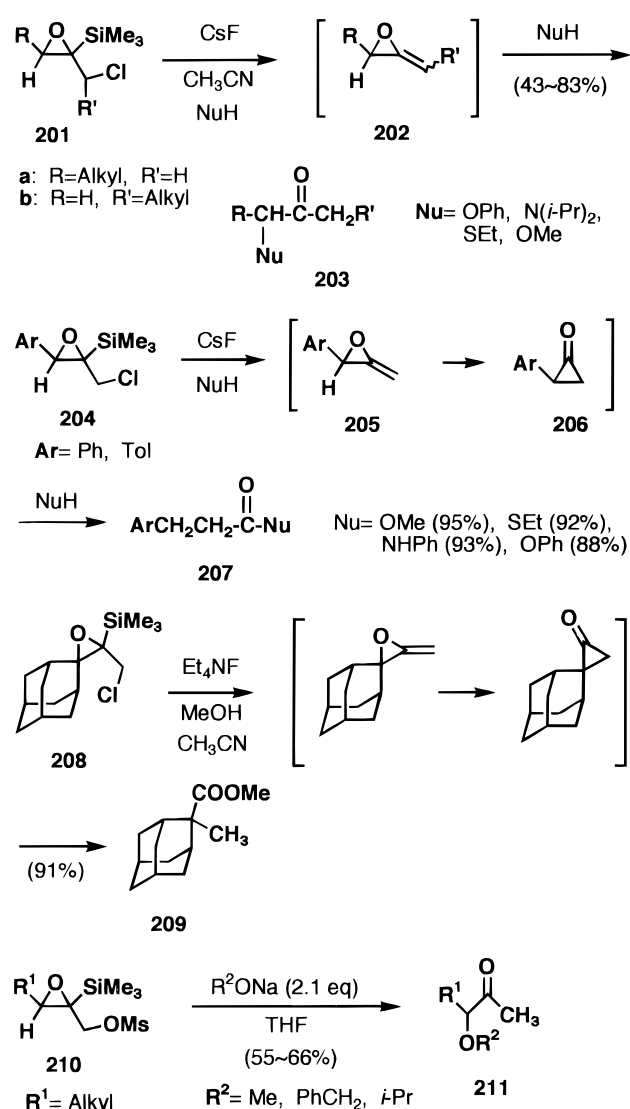


Allene oxide **199** was found to be stable at 25 °C for 1.5 h. Protic nucleophiles react regioselectively with **199** at the carbon-1 position to give α -substituted ketones **200** in good yield.

This procedure was extended to several other epoxy silanes **201** and α -substituted ketones **203** were obtained in good yield (Scheme 31).^{47,48} As long as the R of **201** is an alkyl group or hydrogen, the generated allene oxide **202** reacts at the carbon-1 position with nucleophiles.

In the case of the epoxy silanes having an aryl group **204**, a dramatic change in the course of the

Scheme 31

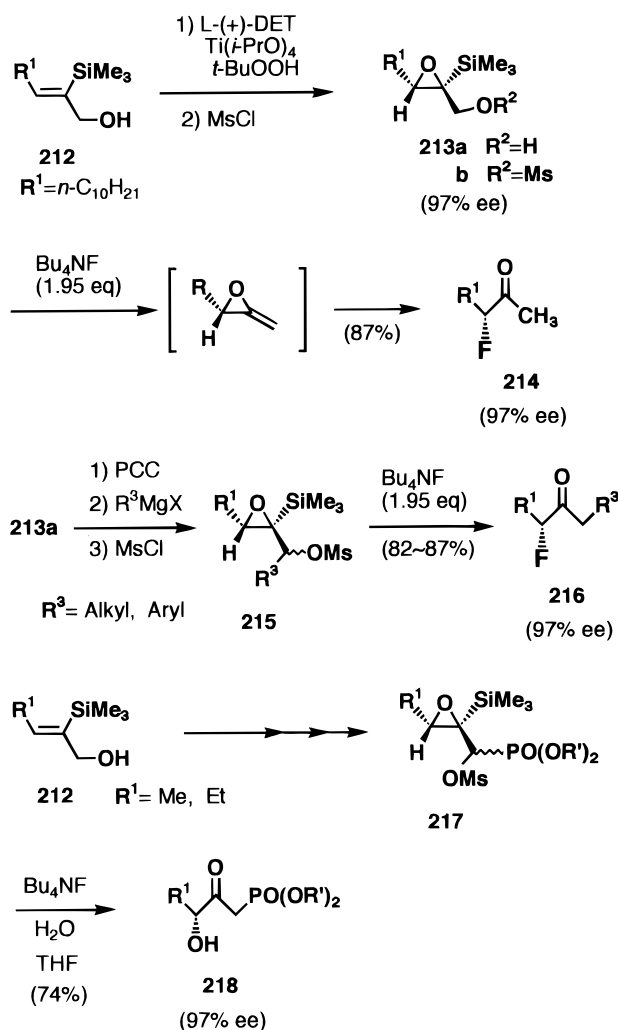


reaction occurred. Treatment of **204** with cesium fluoride in the presence of a nucleophile gave a derivative of dihydrocinnamic acid **207** as the sole product in high yield. The product **207** was derived from cyclopropanone intermediate **206** as in the Favorskii rearrangement. The same reaction was observed with **208** and ester **209** was obtained in high yield.⁴⁷ Interestingly, epoxy silane **210** reacted with sodium alkoxide without a fluoride ion to give α -alkoxy ketone **211** in moderate to good yield.⁴⁹

Highly enantioselective synthesis of α -fluoro ketones and α -hydroxy ketones was achieved by use of the above mentioned procedure (Scheme 32).⁵⁰ The Sharpless asymmetric epoxidation³ of allylic alcohol **212** followed by mesylation gave mesylate **213b** in high enantiomeric excess (ee). Mesylate **213b** was treated with 1.95 equiv of tetrabutylammonium fluoride in THF to give α -fluoro ketone **214** via the allene oxide without any loss of stereochemical integrity. However, even a small excess of tetrabutylammonium fluoride promoted racemization.⁵⁰ In a similar manner, α -fluoro ketone **216** was synthesized from **213a** in high overall yield.

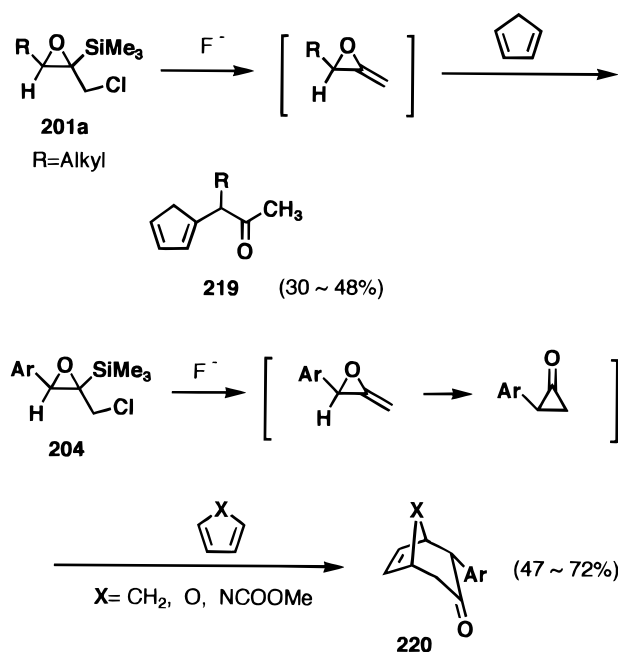
γ -Hydroxy- β -keto phosphonate **218** with high ee was synthesized in good yield from **212** via epoxy silane **217**.⁵¹

Scheme 32



The allene oxide generated by the above-mentioned procedure reacts with cyclopentadiene and related compounds (Scheme 33).^{45a,52,53} When alkyl-substi-

Scheme 33



tuted epoxy silane **201a** was treated with fluoride ion

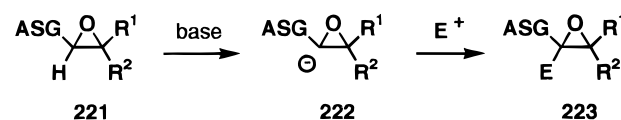
in the presence of cyclopentadiene, substituted product **219** was obtained in low to moderate yield.^{45a,53} Interestingly, aryl-substituted epoxy silane **204** again gave a quite different result. The reaction of **204** with cyclopentadiene, furan, pyrrole, gave 1,4-adduct **220** in good yield. The adduct **220** is expected to be produced from the cyclopropanone.^{45a,52,53}

III. Generation of Oxiranyl Anions and Trapping with Electrophiles

A. Stabilized Oxiranyl Anions

As mentioned in the preceding chapter, oxiranyl anions are usually very unstable. However, when the generated oxiranyl anions have an anion-stabilizing group (ASG) on the α -carbon **222**, they are able to exist from a few minutes to a few hours at low temperature. Moreover, the oxiranyl anions were found to have enough reactivity toward several electrophiles to afford substituted epoxides (Scheme 34).^{54,55}

Scheme 34



Eisch synthesized several epoxides having an ASG **221** and treated them with a strong base at low temperature. The reaction led to the formation of oxiranyl lithium **222** having ASG (stabilized oxiranyl anion) (Table 8).⁵⁴ The oxiranyl lithium **222** reacted with electrophiles such as iodomethane, deuterium oxide, and chlorotrimethylsilane to give substituted epoxide **223** in good yield.

Table 8 summarizes the properties of the stabilized oxiranyl anions **222**. (1) Many stabilized oxiranyl lithiums are able to exist only at about -100°C . (2) As the ASG, second-row elements (Si, P, and S) are effective for stabilizing the oxiranyl anion. (3) An aromatic ring also can be used as the ASG. (4) The rate of the metalation of *cis*-epoxide is faster than that of the *trans*-epoxide. After Eisch's pioneering work on generation of a stabilized oxiranyl anion, several reports were published.

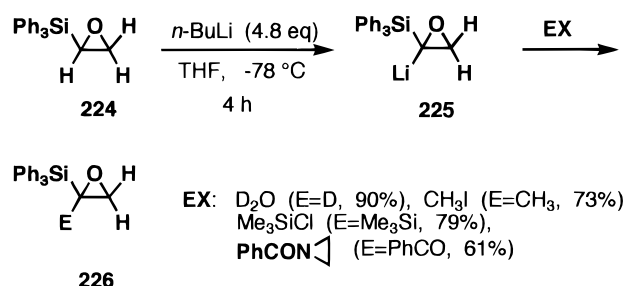
1. Silicon-Stabilized Oxiranyl Anion

Treatment of (epoxyethyl)triphenylsilane (**224**) with 4.5 equiv of *n*-BuLi in THF at -78°C for 4 h led to the formation of oxiranyl lithium **225** (Scheme 35).⁵⁶ Oxiranyl lithium **225** reacted with several electrophiles to afford substituted epoxy silanes **226** in good yields. From these results it was anticipated that the silicon-stabilized oxiranyl lithium **225** would be stable at -78°C for a few hours. Configurational stability of the oxiranyl lithium **225** was assessed using dideuterated epoxy silane **227**. Thus, treatment of **227** with *n*-BuLi followed by water gave dedeuterated epoxide **228** without isomerization of the carbon bearing the triphenylsilyl group.

As already mentioned above, a phenyl group stabilizes the oxiranyl anion. Treatment of **229** with

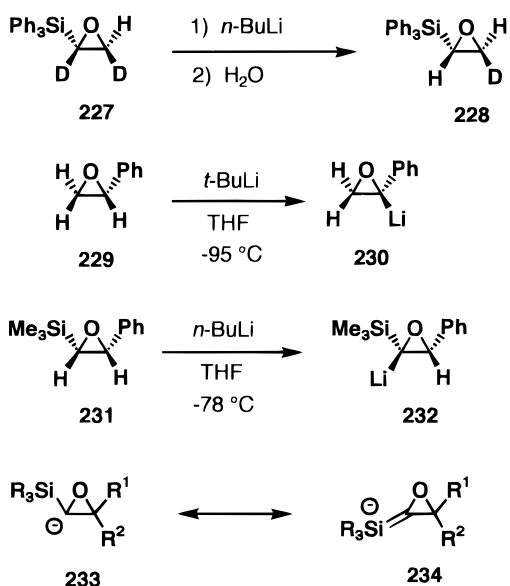
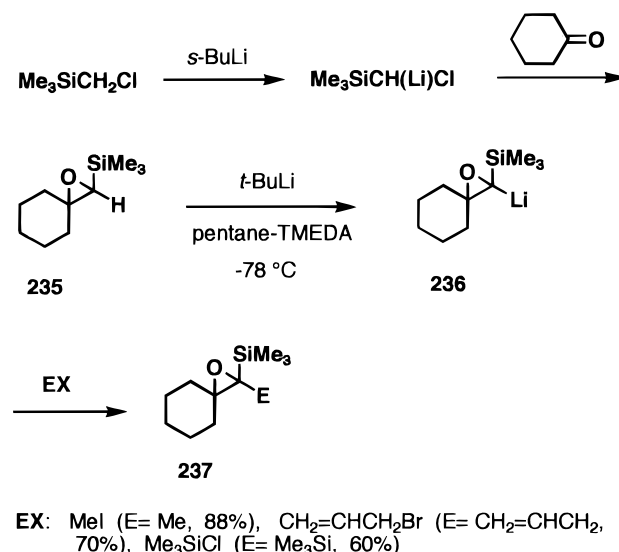
Table 8. Formation of Oxiranyllithium 222 and Trapping with Electrophiles

221			Base	Solvent	Temp / °C	EX	223	
ASG	R ¹	R ²					E	Yield / %
SiPh ₃	H	H	<i>n</i> -BuLi	THF	-78	CH ₃ I	CH ₃	73
SiMe ₃	<i>n</i> -C ₆ H ₁₃	H	<i>t</i> -BuLi - TMEDA	hexane	-90	D ₂ O	D	78
						CH ₃ I	CH ₃	80
SO ₂ Ph	H	<i>n</i> -C ₆ H ₁₃	<i>n</i> -BuLi	THF-hexane-ether	-110	D ₂ O	D	95
						CH ₃ I	CH ₃	96
PO(OEt) ₂	H	H	LDA	"	-110	Me ₃ SiCl	Me ₃ Si	84
						CH ₃ I	CH ₃	37
CN	CH ₃	CH ₃	<i>n</i> -BuLi	"	-110	Me ₃ SiCl	Me ₃ Si	74
CO ₂ Et	CO ₂ Et	H	LDA	"	-110	Me ₃ SiCl	Me ₃ Si	50
Ph	H	H	<i>t</i> -BuLi	THF	-95	Me ₃ SiCl	Me ₃ Si	78

Scheme 35

the silyl group is a more effective ASG than a phenyl group. Some kind of electron withdrawal by silicon was proposed to explain this quite high and somewhat surprising effect of the silyl group on the stabilization of oxiranyllithium, as shown by the resonance between **233** and **234**.⁵⁵

Magnus reported a new method for the synthesis of epoxy silanes and generation of oxiranyllithiums (Scheme 36).⁵⁷ Epoxy silane **235** was synthesized

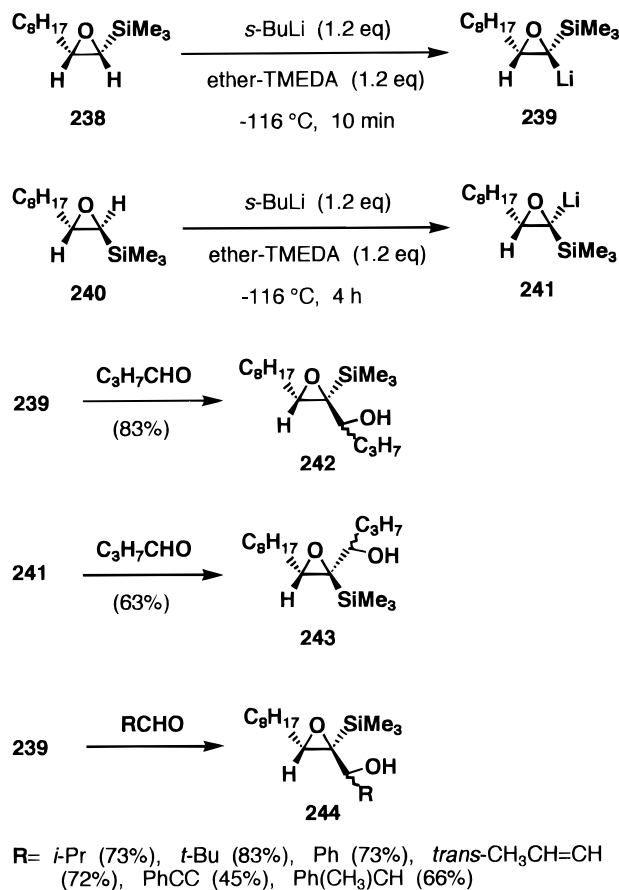
**Scheme 36**

t-BuLi gave oxiranyllithium **230**. Interestingly, lithiation of the epoxide having both silyl and phenyl groups **231** gave oxiranyllithium metalated at the carbon bearing the silyl group, which indicated that

from chloro[(trimethylsilyl)methyl]lithium and cyclohexanone. Lithiation of **235** was performed with *t*-BuLi in pentane at $-78\text{ }^{\circ}\text{C}$ to give **236**, which was treated with electrophiles to afford substituted epoxy silanes **237** in good yield.

Extensive studies for the generation and reaction of silicon-stabilized oxiranyllithium were reported by Molander (Scheme 37).⁵⁸ Treatment of epoxy silane

Scheme 37



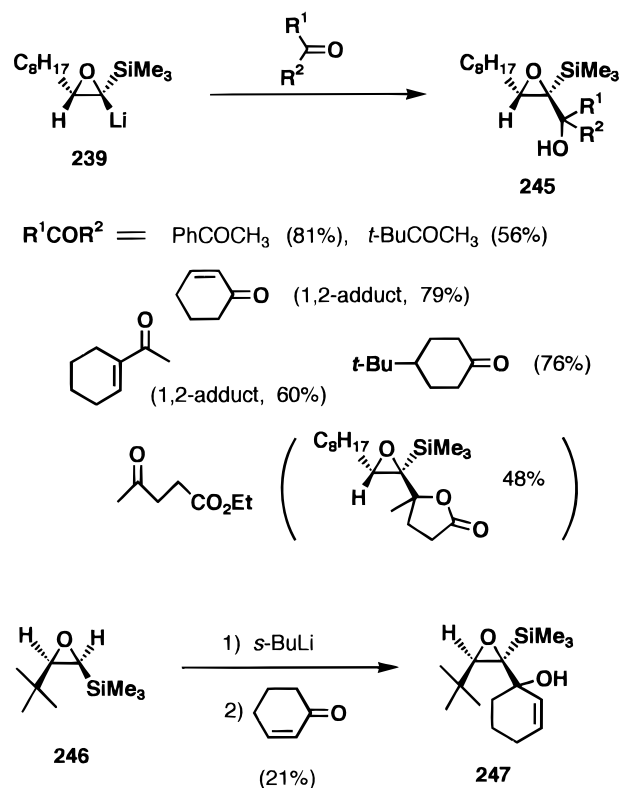
238 with *s*-BuLi in ether in the presence of TMEDA at -116°C gave oxiranyllithium **239** within 10 min. Interestingly, the deprotonation of *trans*-isomer **240** required over 4 h for completion.

The generated oxiranyllithium **239** and **241** reacted with propanal to afford the adducts **242** and **243**, respectively. The adduct **242** and **243** are a mixture of diastereomers; however, the diastereoselectivity is low (2:1 to 1:1.3). These results indicated that trimethylsilyl-substituted oxiranyllithium is stable for periods of hours at -116°C . Treatment of oxiranyllithium **239** with several aldehydes gave the adducts **244** in moderate to good yields, and again, the diastereoselectivities are low (2:1 to 7.7:1).

Oxiranyllithium **239** reacted with various ketones to give adducts **245** in moderate to good yields (Scheme 38). Diastereoselectivity was variable with the ketones used (1.5:1 to 200:1). In the case of α,β -unsaturated ketones, only 1,2-adducts were observed. In all of Molander's experiments, except one example (**246**), complete configurational stability of the oxiranyllithium was observed. One example of configurational inversion was found in the case of **246**. Treatment of **246** with *s*-BuLi followed by 2-cyclohexenone gave the adduct **247** and it was found to be inverted.

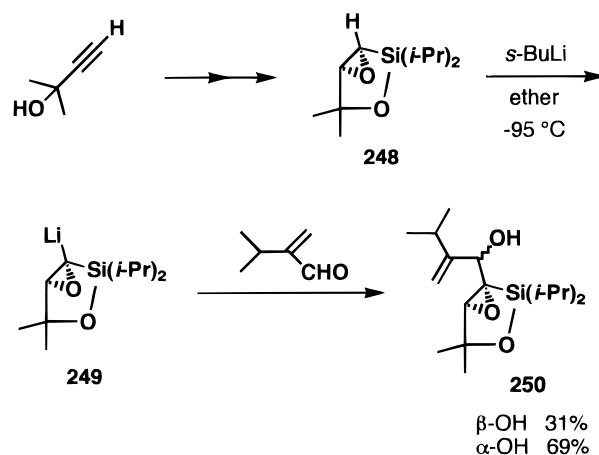
In the context of a total synthesis of spatol, Salomon studied the oxiranyl anion having a temporary bridge **249** to avoid the configurational insta-

Scheme 38



bility of silicon-stabilized oxiranyllithium (Scheme 39).⁵⁹ Lithiation of **248** was carried out with *s*-BuLi

Scheme 39



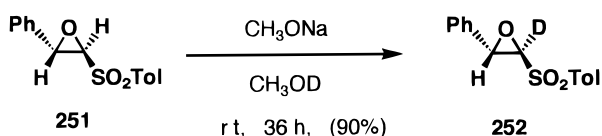
in ether and the generated oxiranyllithium **249** was reacted with 2-isopropylacrolein to give a mixture of diastereomers **250** in high yield. Synthesis of optically active **248** is the objective of his next study.

2. Sulfone-Stabilized Oxiranyl Anions

The first example of the sulfone-stabilized oxiranyl anion was reported by Tavares in his reaction of epoxy sulfone **251** with sodium methoxide in deuteriomethanol, giving deuterated **252** in high yield (Scheme 40).⁶⁰ Eisch also mentioned the sulfone-stabilized oxiranyl anions as already described above.^{54,55}

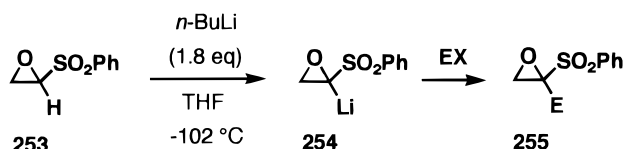
Extensive studies of the formation of sulfone-stabilized oxiranyl anion and trapping with electrophiles were reported by Jackson. Treatment of

Scheme 40

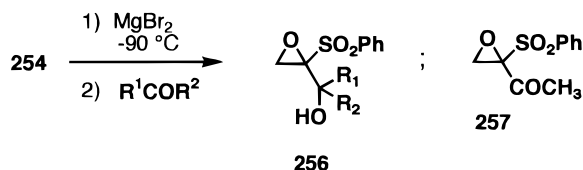


phenylsulfonyl oxirane **253** with $n\text{-BuLi}$ in THF at -102°C gave oxiranyllithium **254** as a pale yellow solution (Scheme 41).^{61,62} Immediately quenching the

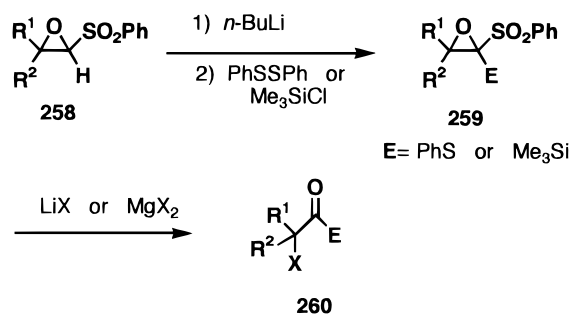
Scheme 41



EX: D_2O ($\text{E}=\text{D}$, 83%), $\text{CH}_2=\text{CHCH}_2\text{Br}$ ($\text{E}=\text{CH}_2=\text{CHCH}_2$, 33%), CH_3I ($\text{E}=\text{CH}_3$, 82%), Me_3SiCl ($\text{E}=\text{Me}_3\text{Si}$, 100%)



R^1COR^2 : Aldehyde (75 ~ 80%), CH_3COCH_3 (67%), cyclopentanone (77%), cyclohexanone (79%), $\text{CH}_3\text{COCH}_2\text{CH}_3$ (78%), $\text{CH}_3\text{COOCH}_3$ (**257**; 55%), $\text{CH}_3\text{CONMe}_2$ (**257**; 48%)



reaction with deuterium oxide at -102°C gave deuterated phenylsulfonyl oxirane **255** ($\text{E}=\text{D}$) in good yield. However, when the solution was allowed to warm above -100°C a substantial amount of polymeric material was formed. These results imply that the sulfone-stabilized oxiranyllithium **254** is quite unstable even at -100°C . In the case of the reaction of **254** with iodomethane or chlorotrimethylsilane, addition of $n\text{-BuLi}$ to a mixture of **253** and electrophile (*in situ* anion quenching) gave a good yield of **255**.

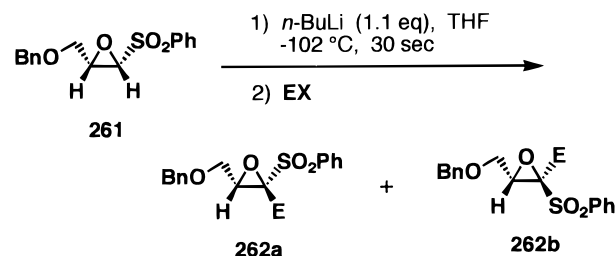
The reaction of **254** with carbonyl compounds was problematical; the anion **254** did not give the adduct **256** with a carbonyl compound. However, in the reaction, addition of magnesium bromide followed by carbonyl compounds gave good yields of the products **256** or **257**. The role of the magnesium bromide is

thought to be a Lewis acid activating the carbonyl compounds toward nucleophilic attack.⁶²

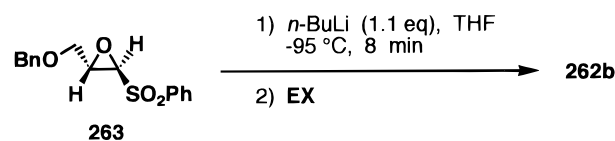
Reaction of the sulfone-stabilized oxiranyllithium derived from **258** with diphenyl disulfide⁶³ and chlorotrimethylsilane⁶⁴ giving **259** was also reported. From the synthetic point of view, **259** is a good precursor for synthesis of α -halo thio esters and α -halo acylsilanes **260**.^{63,64}

The oxiranyllithium generated from functionalized epoxy sulfones **261** and **263** showed different stability and reactivity (Scheme 42).^{62,65} Metalation of **261**

Scheme 42



EX: D_2O (85%), TMSCl (63%), CH_3I (71%), PhCHO (63%)



EX: D_2O (80%), TMSCl (80%), CH_3I (87%), PhCHO (87%)

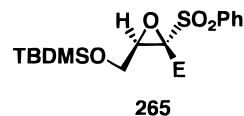
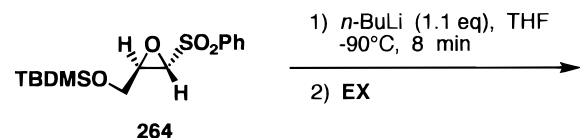
with $n\text{-BuLi}$ occurred at -102°C within 30 s. Immediate addition of electrophiles afforded the substituted product **262a** with the isomerized product **262b** (less than 5% yield). Delaying the addition of electrophiles to 3 min, the yield of **262a** was reduced and the yield of **262b** increased. These results show that the oxiranyl anion generated from **261** is quite unstable and also is configurationally unstable.

In contrast with **261**, the metalation of *trans*-isomer **263** required 8 min at -95°C for completion. Reaction of the generated oxiranyllithium with electrophiles gave **262b** as the sole product, and the yields were better than that from the reaction of **261**. These results show that the anion from **263** is much more stable and also is configurationally stable.

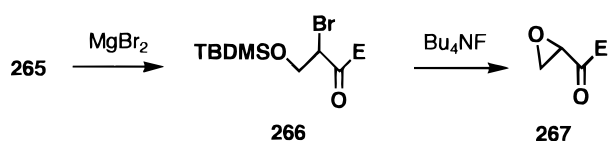
For synthetic purposes, Jackson synthesized **264** (Scheme 43).^{62,65,66} Metalation of **264** cleanly gave relatively stable oxiranyllithium, which reacted with several kinds of electrophiles to give **265** in good to excellent yields. The product **265** was transformed to α -bromo ketone **266** by treating with magnesium bromide. Deprotection of the TBDMS group with tetrabutylammonium fluoride directly afforded α,β -epoxy ketone **267**. This procedure offers a good method for synthesizing epoxy ketones.

Jackson planned to lithiate the sulfoximinooxirane **268** under the similar conditions as above. However, the trial was unsuccessful even at -108°C due to the greater instability of lithiated sulfoximinoox-

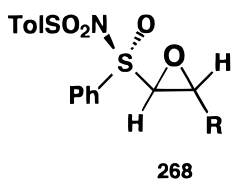
Scheme 43



EX: D₂O (85%), TMSCl (84%), CH₃I (79%), PhCH=CHCH₂Br (93%), C₅H₁₁I (98%), CH₃CHO (85%), PhCHO (83%), cyclohexanone (98%), CH₃OCOCi (77%), *i*-BuCOCl (76%), CH₃COOCH₃ (61%), PhSSPh (76%), etc.

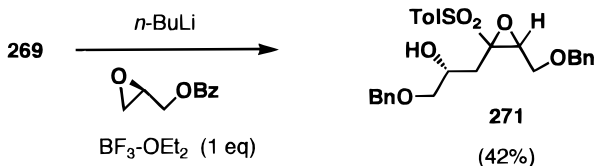
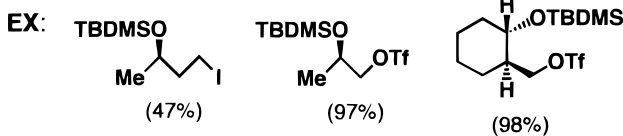
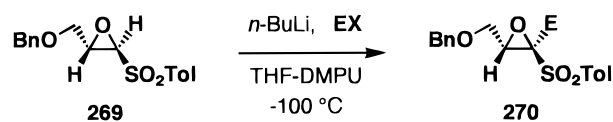


oxiranes compared with the corresponding lithiated sulfonyloxiranes.⁶⁷

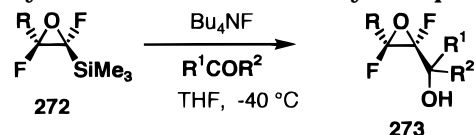


Very recently, Mori used the above-mentioned chemistry in his synthesis of highly oxygenated complex materials (Scheme 44).⁶⁸ Treatment of **269**

Scheme 44



with *n*-BuLi in a mixture of THF-*N,N'*-dimethylpropyleneurea (DMPU) at -100 °C led to the formation of oxiranyllithium within a few minutes. Reaction of the oxiranyllithium with electrophiles gave the alkylated product **270** in high yields. Alkyl triflates were found to be better electrophiles than alkyl iodides in this reaction. Interestingly, epoxide

Table 9. Fluoride Ion Promoted Reaction of Fluorosilyloxiranes **272** with Carbonyl Compounds

272		Adduct 273	
R	R ¹	R ²	Yield / %
<i>n</i> -Hep	CH ₃	H	85
	Pr	H	65
	Ph	H	70
<i>s</i> -Bu	CH ₃	CH ₃	48
	Ph	CH ₃	48
<i>t</i> -Bu	CH ₃	H (1,2-add.)	63
	Ph	CH ₃	48

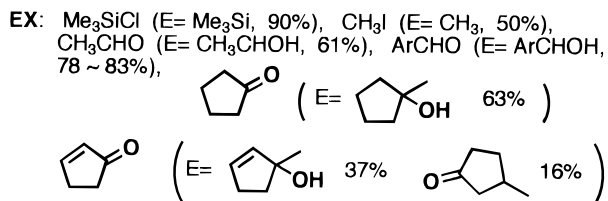
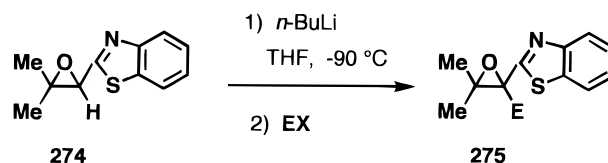
reacted with the oxiranyllithium in the presence of 1 equiv of BF₃-etherate to afford **271** as a 1:1 mixture of diastereomers, though the yield was moderate.

3. Other Stabilized Oxiranyl Anions

Treatment of epoxy silane bearing fluorine as an ASG **272** with tetrabutylammonium fluoride gave a fluorine-stabilized oxiranyl anion (Table 9).⁶⁹ When this reaction was carried out with aldehydes or ketones, moderate to good yield of the adduct **273** was obtained.

Lithiation of benzothiazolyl-substituted epoxide **274** with *n*-BuLi or LDA in THF at -90 °C gave benzothiazole-stabilized oxiranyllithium as a dark-red solution (Scheme 45).⁷⁰ The generated oxiranyl-

Scheme 45

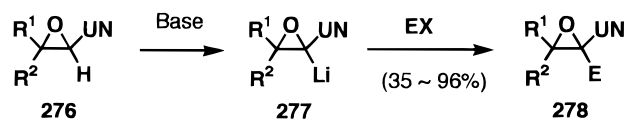


lithium reacted with several electrophiles to give **275** in moderate to good yields. In the case of the reaction with cyclopentenone, a mixture of 1,2- and 1,4-addition products was obtained. Moreover, the benzothiazole-stabilized oxiranyllithium was found to be configurationally unstable.

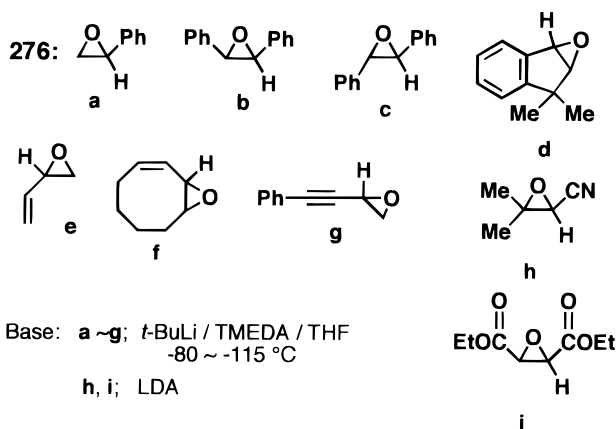
The phenyl group is already mentioned as an ASG in oxiranyl anion (see Table 8).⁵⁴ Eisch reported

extensive study on the unsaturated organyl group-stabilized oxiranyl anion **277** (Scheme 46).⁷¹ Treat-

Scheme 46



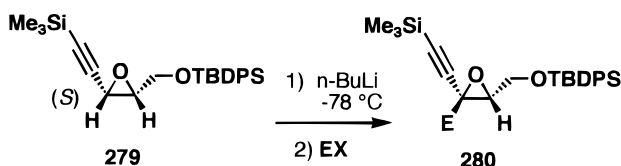
UN indicates an unsaturated organyl group



ment of **276** in THF with 1:1 complex of *t*-BuLi and TMEDA at –115 to –80 °C gave oxiranyl lithium **277**. The epoxides **276a–g** gave oxiranyl lithium **277** by lithium–hydrogen exchange of the depicted proton. In the case of **276h** and **276i** LDA was used as a base. The generated oxiranyl lithium reacted with electrophiles to give **278** in variable yields.

Optically pure trisubstituted ethynylloxirane **280** was synthesized from **279** by the above-mentioned chemistry (Scheme 47).⁷² Lithiation of **279** was

Scheme 47



EX: Me₃SiCl (96%), CH₃I (81%), *n*-C₆H₁₃CHO (97%), CH₃SO₂Cl (0%)

achieved with *n*-BuLi at –78 °C, and the generated oxiranyl lithium was reacted with electrophiles to give **280** in high yields, except in one case. The optical purity of **280** was found to be perfect.

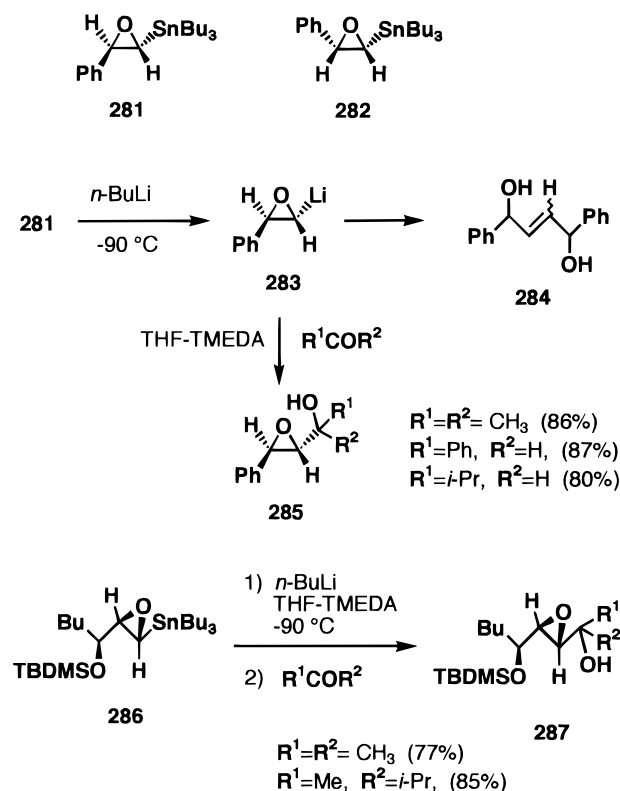
B. Nonstabilized Oxiranyl Anions and Destabilized Oxiranyl Anions

As already described, oxiranyl anions are quite unstable even at low temperature. Quick reactions at very low temperature are required for generation of oxiranyl anions. Metal–hydrogen exchange reaction is obviously not useful for generation of nonstabilized oxiranyl anions and destabilized oxiranyl anions.

Only one example has been published so far of generation and reaction of a nonstabilized oxiranyl-

lithium (Scheme 48).⁷³ Treatment of **281** with *n*-BuLi

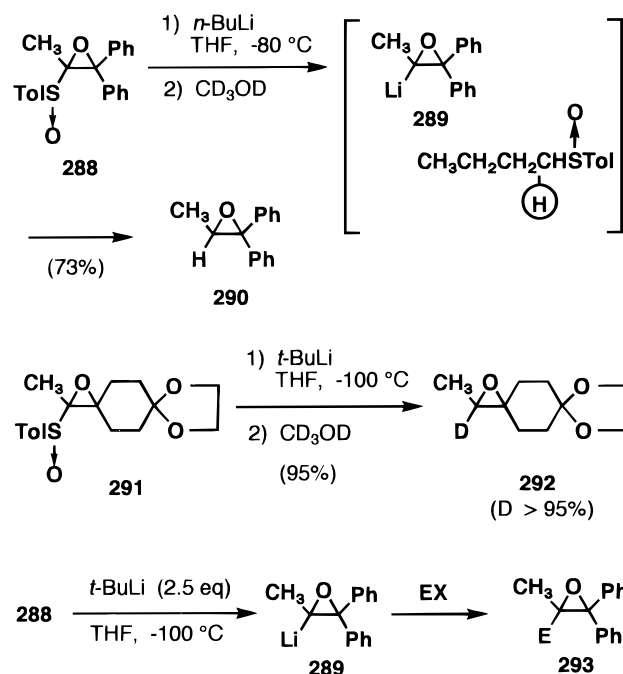
Scheme 48



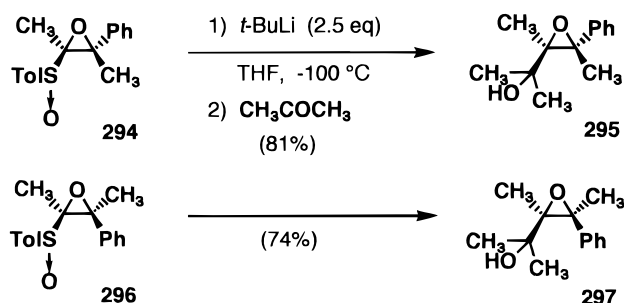
in THF at –90 °C led to the formation of nonstabilized oxiranyl lithium **283** within 5 min via tin–lithium exchange. Reaction of **283** with carbonyl compounds, however, gave low yield of the adduct with a significant amount of dimer **284**. The amount of this byproduct was reduced by the addition of 2 equiv of TMEDA in the reaction mixture. Under these conditions the desired adduct **285** was obtained in good yield. The *cis*-isomer **282** gave the corresponding adduct via nonstabilized oxiranyl lithium in somewhat lower yields (70–72%). Similar treatment of optically active epoxy stannane **286** gave optically active **287** in good yield.

Recently, the first example of destabilized oxiranyl lithium and oxiranyl Grignard reagent was reported by us (Scheme 49).⁷⁴ Sulfinyloxirane **288** was treated with *n*-BuLi in THF at –80 °C for 1 min, and then the reaction was quenched with methanol-*d*₄ to afford desulfinylated epoxide **290**; however, no deuterium incorporation was observed. Obviously, this reaction proceeds via oxiranyl lithium **289**. The reason why the product has no deuterium is explained as follows. Ligand exchange reaction of sulfoxide of **288** with *n*-BuLi³⁶ takes place as the first reaction to give oxiranyl lithium **289** and butyl *p*-tolyl sulfoxide. Because the sulfoxide has acidic hydrogen (depicted in Scheme 49), generated **289** quickly picks up the acidic hydrogen to afford **290** before the methanol-*d*₄ quenching. Actually, the reaction of **291** with *t*-BuLi at –100 °C followed by immediate quenching with methanol-*d*₄ gave deuterated epoxide **292** in high yield and high deuterium incorporation. In this reaction, the generated *tert*-butyl *p*-tolyl sulfoxide has no acidic hydrogen. The ligand exchange reaction of sulfoxide of sulfinyloxiranes is

Scheme 49



EX: CH₃CH₂CHO (80%), cyclohexanone (83%), Me₃SiCl (82%), EtOCOCI (E= EtOCO, 87%), Et₂NCOCl (E= Et₂NCO, 66%), CH₃COIm (E=CH₃CO, 28%)

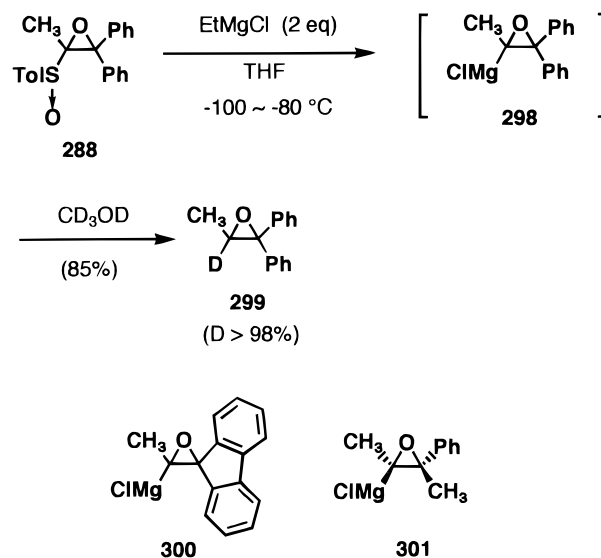


found to be quite rapid; it is complete within a few seconds. This reaction evidently is one of the best ways for generation of oxiranyl anions.

The generated oxiranyl lithium **289** is very unstable even at -100 °C; however, the destabilized oxiranyl lithium **289** has enough reactivity toward various kinds of electrophiles to afford substituted epoxide **293**. Moreover, the destabilized oxiranyl lithium was found to be configurationally stable at -100 °C. For example, sulfinyloxiranes **294** and **296**, derived from acetophenone, gave the adduct **295** and **297**, respectively, without any detectable isomers.

The first example of an oxiranyl Grignard reagent was also reported in the same paper (Scheme 50).⁷⁴ Treatment of **288** with ethylmagnesium chloride followed by methanol-*d*₄ gave deuterated epoxide **299** in good yield with excellent deuterium incorporation. The oxiranyl Grignard reagent **298** was found to be more stable than the corresponding oxiranyl lithium. However, the oxiranyl Grignard reagent was found to be unreactive, failing to react even with aldehyde. Other oxiranyl Grignard reagents **300** and **301** were synthesized from the corresponding sulfinyloxiranes with ethylmagnesium chloride.

Scheme 50



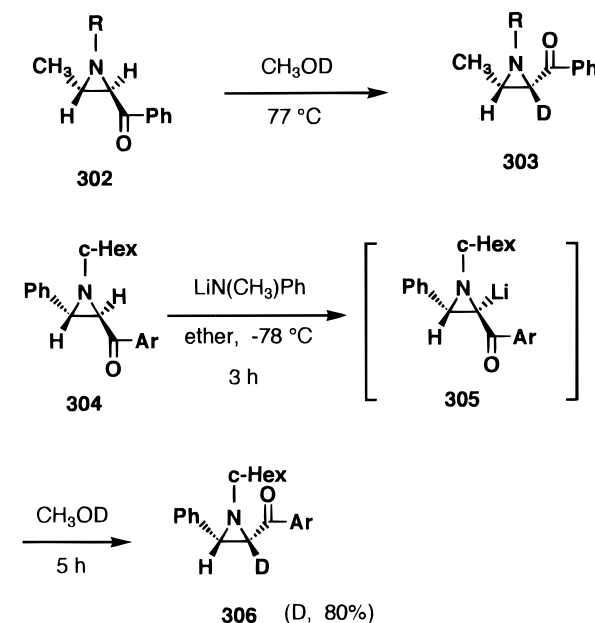
IV. Aziridinyl Anions

In contrast to the wide range of studies on the chemistry of oxiranyl anions, very limited work on aziridinyl anions has so far been published. However, from such work we now recognize that many aziridinyl anions are unexpectedly stable. The chemistry of aziridinyl anions will hereinafter be described.

A. Stabilized Aziridinyl Anions

Padwa reported that heating *trans*-aziridinyl ketone **302** in deuteriomethanol at 77 °C led to the formation of *cis*-aziridinyl ketone having a deuterium atom on the aziridine ring **303** (Scheme 51).⁷⁵ A

Scheme 51



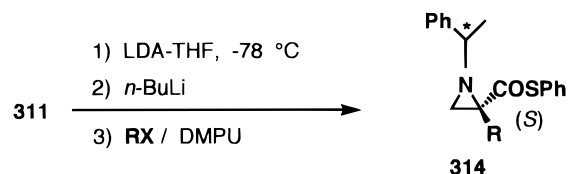
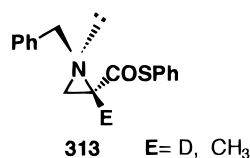
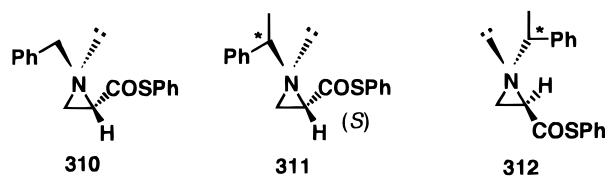
similar study was carried out by Cromwell.⁷⁶ Treatment of *trans*-aziridinyl ketone **304** with lithium *N*-methylanilide in ether at -78 °C followed by deuteriomethanol gave *cis*-deuterioaziridinyl ketone **306**. The intermediate of this reaction was proposed to be

aziridinyl lithium **305**. From the results, the aziridinyl anion is expected to be stable. Moreover, the aziridinyl lithium **305** is configurationally unstable and *cis*-aziridine is thermodynamically more stable.

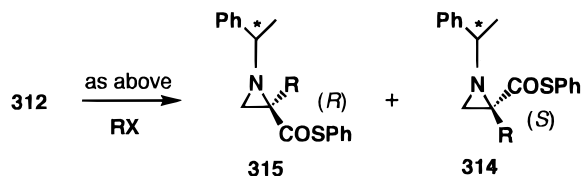
Generation of aziridinyl lithium of phenylthio aziridine carboxylates **307** and trapping with electrophiles was reported by Seebach (Table 10).^{77,78} Treatment of the thiol ester **307** with LDA at $-78\text{ }^{\circ}\text{C}$ for 30 min followed by addition of electrophiles at $-100\text{ }^{\circ}\text{C}$ led to the formation of **309** in good yields and moderate diastereoselectivities. In the case with iodomethane and benzyl bromide, DMPU was required as a cosolvent. Without DMPU, only the starting material and decomposition products were obtained.

Seebach synthesized nonracemic aziridines **310**–**312** in order to gain information on the structure of small-ring ester enolates and to develop methodology for synthesis of enantiomerically pure aziridines (Scheme 52).⁷⁸ Treatment of **310** with LDA-*n*-BuLi

Scheme 52

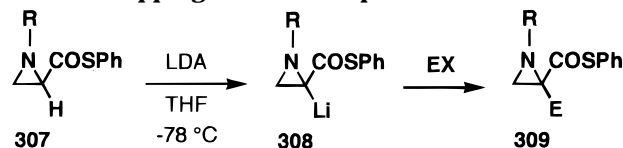


RX: CH_3I (62%), $\text{CH}_3\text{CH}_2\text{I}$ (51%), $\text{CH}_2=\text{CHCH}_2\text{Br}$ (59%), PhCH_2Br (60%), $\text{PhCH}=\text{CHNO}_2$ (1,4-adduct, 79%)



RX: CH_3I (R = CH_3 , 51%, **315** : **314** = 4 : 1)
 PhCH_2Br (R = PhCH_2 , 57%, **315** : **314** = 2 : 1)

followed by methanol- d_4 or iodomethane–DMPU gave optically active **313** and the results showed that the reaction proceeded with retention of stereochemistry at the carbon bearing the thiolester. The aziridinyl lithium generated from **311** reacted with several alkyl halides to give substituted products **314**, again with retention of the configuration. However, configurational instability was observed in the case of the reaction of **312** with alkyl halides. Reaction of **312** with alkyl halides under the same conditions as

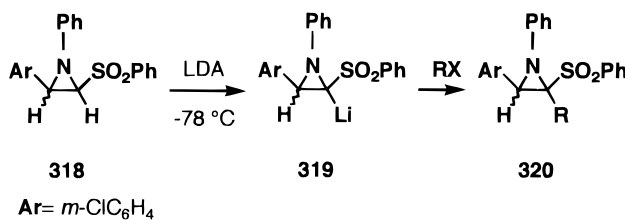
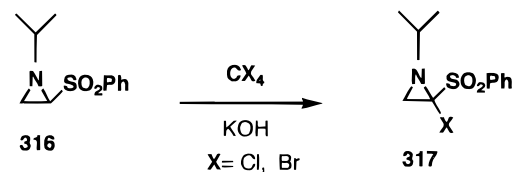
Table 10. Generation of Aziridinyl Lithium **308** from **307** and Trapping with Electrophiles

307 R	EX	309	
		E	Yield / %
<i>t</i> -Bu	CH_3CHO	$\text{CH}_3\text{CH}(\text{OH})$	70
	PhCHO	$\text{PhCH}(\text{OH})$	87
	$\text{Ph}-\text{CH}=\text{CH}-\text{NO}_2$	$\text{PhCHCH}_2\text{NO}_2$	75
CH ₃ (DMPU)	CH ₃	CH ₃	60
			60
Bn	PhCHO	$\text{PhCH}(\text{OH})$	71
	CH ₃ (DMPU)	CH ₃	61
	PhCH_2Br (DMPU)	PhCH_2	62

above gave a mixture of **315** and **314**. Seebach extensively discussed the interpretation of these results; however, the problem of the configurational stability of aziridinyl anions at present remains unresolved.

Carbon tetrahalides reacted with 2-(phenylsulfonyl)aziridine **316** to afford 2-(phenylsulfonyl)-2-haloaziridine **317** (Scheme 53).⁷⁹ Reutrakul reported

Scheme 53

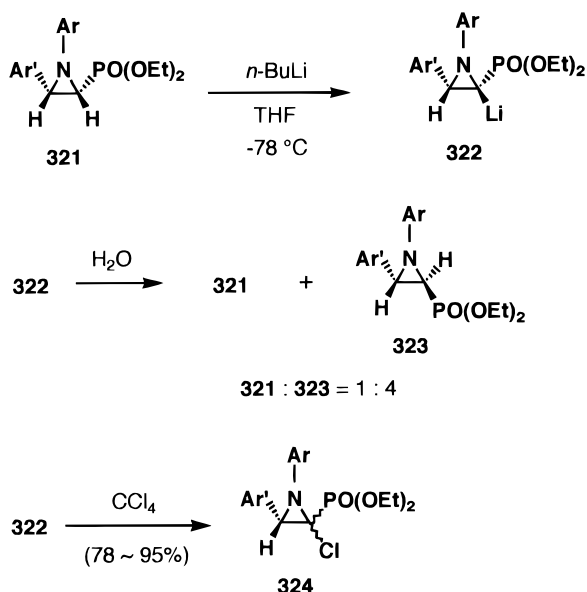


R = CH_3 (100%), $\text{CH}_2=\text{CHCH}_2$ (78%), PhCH_2 (71%), $\text{PhCH}=\text{CHCH}_2$ (100%)

alkylation of 2-(phenylsulfonyl)aziridine **318** via aziridinyl lithium **319**.⁸⁰ Thus, treatment of **318** with LDA in THF at $-78\text{ }^{\circ}\text{C}$ gave a dark-green solution of the aziridinyl lithium **319**. Addition of an alkyl halide to the reaction mixture led to the formation of alkylated aziridine **320** in good yield.

Aziridinyl lithium **322** was generated from aziridinylphosphonate **321** with *n*-BuLi in THF as a dark-red solution (Scheme 54).⁸¹ Quenching **322** with water gave **321** and isomerized **323** in a ratio of 1:4. This result shows that the configurational stability of **322** is low. Moreover, reaction of **322** with several electrophiles (such as iodomethane and aldehydes)

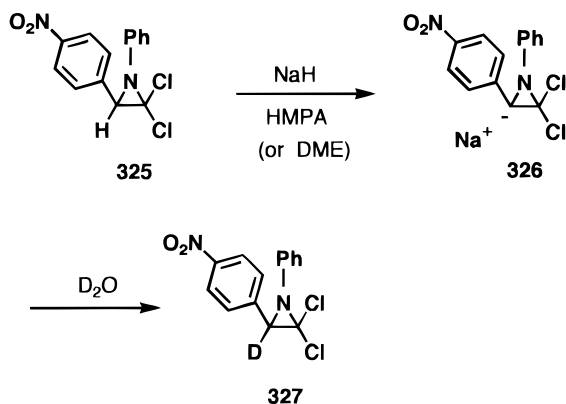
Scheme 54



totally failed. The only one successful reaction was chlorination with carbon tetrachloride, giving **324**. These results point to some different property of the lithiated aziridinylphosphonate **322** compared to the aziridinyl lithium **319** from phenylsulfonyl aziridine **318**, which was alkylated under a similar conditions in good yield (see Scheme 53).

In 1972, Rubottom and Stevenson described for the first time the preparation of *p*-nitrophenyl-stabilized aziridinyl anion **326** from aziridine **325** and sodium hydride (Scheme 55).⁸² The aziridinyl anion **326** was

Scheme 55

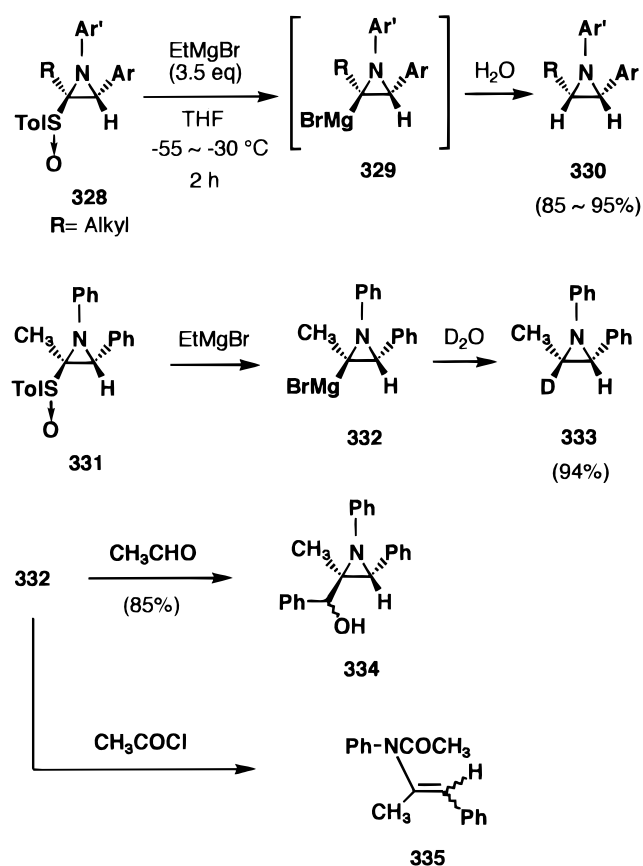


the first example of a stable aziridinyl C-anion. When **325** was treated with sodium hydride in HMPA (or DME) the anion **326** was formed as a bright purple solution. Quenching of **326** with deuterium oxide gave deuterated aziridine **327**. The anion **326** was found to be surprisingly stable. After 3 days at $-10\text{ }^\circ\text{C}$ in HMPA, **326** gave **327** in 66% yield upon quenching with deuterium oxide.

B. Nonstabilized Aziridinyl Anions

Only four papers have so far been published on generation of nonstabilized aziridinyl anions. In 1988, the present author reported the first example of nonstabilized (or destabilized) aziridinyl anion **329** from sulfinylaziridine **328** with alkylmetals via stereospecific desulfinylation (Scheme 56).⁸³ Desulfinyl-

Scheme 56

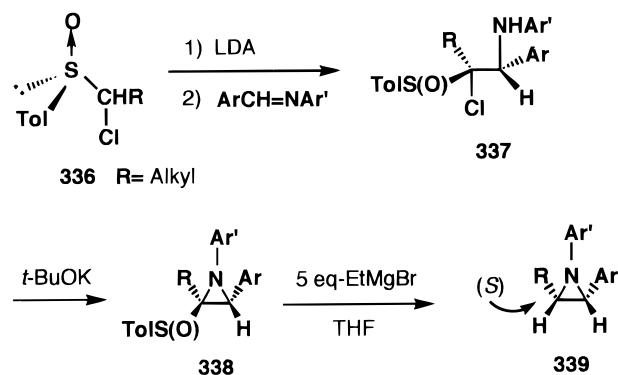


ation of sulfinylaziridine **328** with several alkylmetals was investigated and it was found that ethylmagnesium bromide was the reagent of choice. $n\text{-BuLi}$ and methyllithium were also effective for the desulfinylation. After treatment of **328** with 3.5 equiv of ethylmagnesium bromide in THF, the generated aziridinyl Grignard reagent **329** was protonated with water to afford aziridine **330** in high yield with complete retention of the carbon bearing the sulfinyl group.

Treatment of **331** with ethylmagnesium bromide followed by deuterium oxide led to the formation of deuterated aziridine **333** with high deuterium incorporation.⁸⁴ The aziridinyl Grignard reagent **332** was found to be very stable; allowing **332** to stand at $0\text{ }^\circ\text{C}$ for 1 h followed by quenching with deuterium oxide gave **333** without lowering the chemical yield or the deuterium incorporation. However, the aziridinyl Grignard reagent **332** was found to have low reactivity with several electrophiles. For example, **332** reacted with only acetaldehyde, not with ketones, to give adduct **334** as a mixture of diastereomers. With acetyl chloride, **332** gave enamide **335** in low yield as the only isolable product.

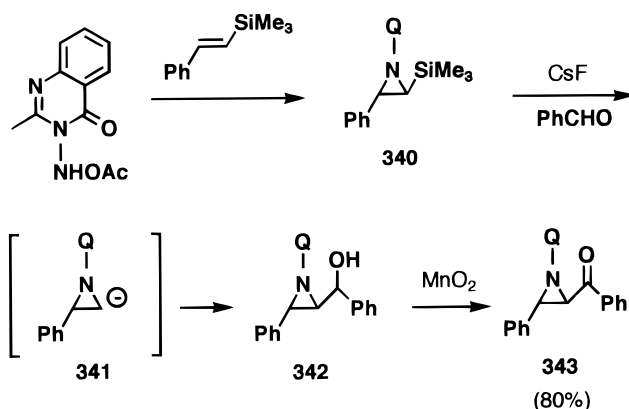
The procedure mentioned above was extended to a chiral synthesis of aziridines (Scheme 57).⁸⁴ The carbanion of optically active 1-chloroalkyl *p*-tolyl sulfoxide (**336**) reacted with imines to give optically active chloroamine **337** with full 1,2- and 1,3-asymmetric induction. Treatment of **337** with potassium *tert*-butoxide gave optically pure sulfinylaziridine **338**. Stereospecific desulfinylation of **338** was carried out with 5 equiv of ethylmagnesium bromide in THF to afford optically pure (–)-(*Z*)-*N*-arylaziridine **339** in almost quantitative yield.

Scheme 57



Aziridinyl anion **341** from aziridinyllithium **340** was reported by Atkinson (Scheme 58).⁸⁵ Aziridinyllithium

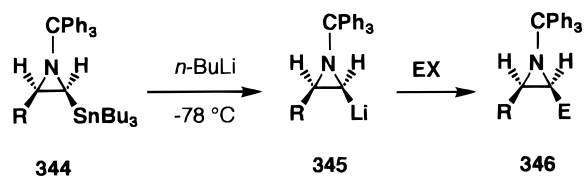
Scheme 58



340 was prepared by the reaction of *N*-acetoxyaminoquinazolinone with alkenylsilane. Treatment of **340** with cesium fluoride in DMF in the presence of 3 equiv of benzaldehyde at room temperature gave a labile product **342**, which was immediately oxidized with manganese dioxide to give benzoylaziridine **343** in good yield.

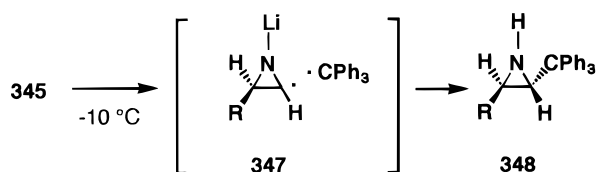
Nonstabilized aziridinyl lithium **345** was prepared from aziridinyltin **344** by tin–lithium exchange (Scheme 59).⁸⁶ Treatment of **344b** with *n*-BuLi in

Scheme 59



a: R= Me: EX= CH₃OH (E=H, 92%), D₂O (E=D, 85%; 97%-D), PhCHO (E=PhCH(OH), 66%)

b: R= CH₂OMOM: EX= D₂O (E=D, 84%), EtOCOCl (E=CO₂Et, 64%), C₂Cl₆ (E=Cl, 92%), PhCHO (E=PhCH(OH), 81%)



THF at $-78\text{ }^{\circ}\text{C}$ for 15 min resulted in tin–lithium exchange to afford aziridinyl lithium **345b**. The lithiation of **344a** required harsher conditions ($-60\text{ }^{\circ}\text{C}$ followed by brief warming to $-10\text{ }^{\circ}\text{C}$) for completion of the reaction. The so-generated aziridinyl lithium **345** reacted with typical electrophiles to give **346** in good to excellent yields. The results indicate that **345** is stable below $-10\text{ }^{\circ}\text{C}$ and is configurationally stable.

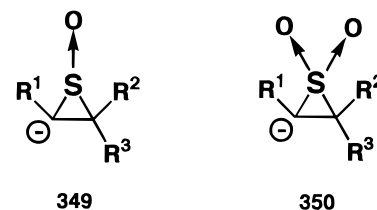
Warming **345** from $-10\text{ }^{\circ}\text{C}$ to room temperature led to the formation of *trans*-2,3-disubstituted aziridine **348**. A caged radical–radical anion pair **347** was suggested as the intermediate of this reaction.

V. Conclusions and Perspective

As outlined in this review, oxiranyl anions are quite unstable. Generation of the oxiranyl anions at around room temperature leads to the formation of β -oxido carbenoids, which afford various kinds of products such as ketones, aldehydes, olefins, and the products from C–H insertion. Some oxiranyl anions, especially those having an anion-stabilizing functional group (stabilized oxiranyl anions) can be generated by hydrogen–lithium exchange reaction at below $-78\text{ }^{\circ}\text{C}$. Nonstabilized and destabilized oxiranyl anions also can be generated by tin–lithium exchange or ligand exchange reaction of sulfoxides with alkylmetals at around $-100\text{ }^{\circ}\text{C}$. The generated oxiranyl anions react with various electrophiles to give substituted epoxides. This method is useful for synthesis, including asymmetric synthesis, of epoxides and it is expected that many more new procedures will be forthcoming.

In contrast to the oxiranyl anions, aziridinyl anions are much more stable. However, very limited reports have appeared so far. For this reason the nature, stability, and reactivity of aziridinyl anions are still somewhat obscure at present. Because aziridines are very useful in synthetic organic chemistry, more studies should be continued for the elucidation of the chemistry of aziridinyl anions.

Although a few reports on the chemistry of episulfoxide α -anions **349**⁸⁷ and episulfone α -anions **350**,⁸⁸ the sulfur analogs of oxiranyl anions, were published the present author did not describe them in this review; only recent papers are listed.



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