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Generation of Oxiranyllithiums and Oxiranyl Grignard Reagents Having a Carbanion-Destabilizing Group from Sulfinyloxiranes: Their Property and an Application to Asymmetric Synthesis of Epoxides and Alcohols

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Abstract: The first generation of oxiranyllithiums and oxiranyl Grignard reagents having a carbanion-destabilizing group (alkyl group) was realized from sulfinyloxiranes via the ligand exchange reaction of sulfoxides with *tert*-butyllithium or ethylmagnesium chloride in THF at -80 to -100 °C. The generated oxiranyllithiums were found to be very unstable; however, these anions reacted with several electrophiles to give epoxides in up to 86% yield. The oxiranyl Grignard reagents were found to be more stable and much less reactive than the oxiranyllithiums. The reactivities of the oxiranyllithiums having several alkyl groups were investigated. As an application of the method, optically active tri- and tetra-substituted epoxides and alcohols were synthesized from optically active chloromethyl *p*-tolyl sulfoxide via the oxiranyllithiums.

Epoxides are widely recognized as being extremely versatile synthetic intermediates.[1] The reaction of epoxides with a variety of nucleophiles leads to ring openings under both acidic and basic conditions. Carbon-carbon and carbon-heteroatom bond-formation, Lewis acid- or base-promoted isomerization and rearrangement[2] are of value in organic synthesis and innumerable studies have been published for their use in organic synthesis. In these reactions the epoxides act as electrophiles **1**. On the other hand, the reactions in which epoxides act as nucleophiles are quite limited. One such epoxide is a carbanion of epoxide, named oxiranyl anion **2**.[3] However, oxiranyl anions themselves have been known to be very unstable and have rarely been used in carbon-carbon bond-formation reactions.[3]

Generation of oxiranyllithiums from epoxysilanes by lithium-hydrogen exchange and trapping them with some electrophiles was first reported by Eisch in 1976.[4] Since then, silicon-stabilized oxiranyl anions,[5] fluorine-stabilized oxiranyl anions,[6] unsaturated group-stabilized oxiranyl anions,[7] and sulfone-stabilized oxiranyl anions[8] were reported. In particular, sulfone-stabilized oxiranyllithiums were extensively studied by Jackson[8] and the chemistry was applied to a synthesis of complex natural products by Mori and Furukawa.[9]

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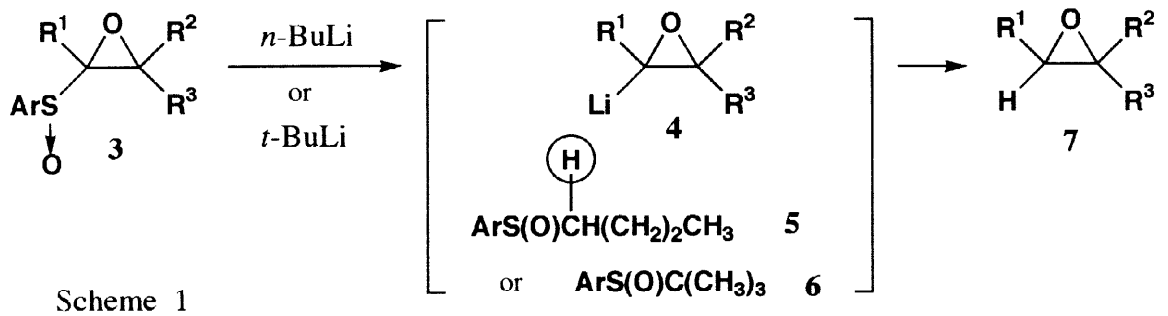
These oxiranyl anions are called *stabilized oxiranyl anion* (**2**: R = carbanion stabilizing group). Oxiranyl anions having hydrogen (**2**: R = H) are called *non-stabilized oxiranyl anion* and they were generated from oxiranyltins via tin-lithium exchange by Pfaltz in 1991.[10]

In 1995 we reported for the first time an example of *destabilized oxiranyl anions* (**2**: R = carbanion destabilizing group)[11] from sulfinyloxiranes **3** by the ligand exchange reaction of sulfoxides.[12] In this paper we report in detail the generation of destabilized oxiranyllithiums and oxiranyl Grignard reagents, their properties and some synthetic applications.

Results and Discussion

In previous papers we reported a stereospecific desulfinylation of sulfinyloxiranes **3** with *n*-BuLi to afford epoxides **7** (Scheme 1).[13] In the reaction, the intermediate was assumed to be oxiranyllithium **4**. We proposed the mechanism of this reaction as follows.[13b] This reaction gives **4** and aryl butyl sulfoxide **5** via the ligand exchange reaction of sulfoxide. The oxiranyllithium **4** quickly picks up the acidic α-hydrogen of the sulfoxide **5** to give epoxide **7** in high yield even though **4** is known to be very unstable.



Scheme 1

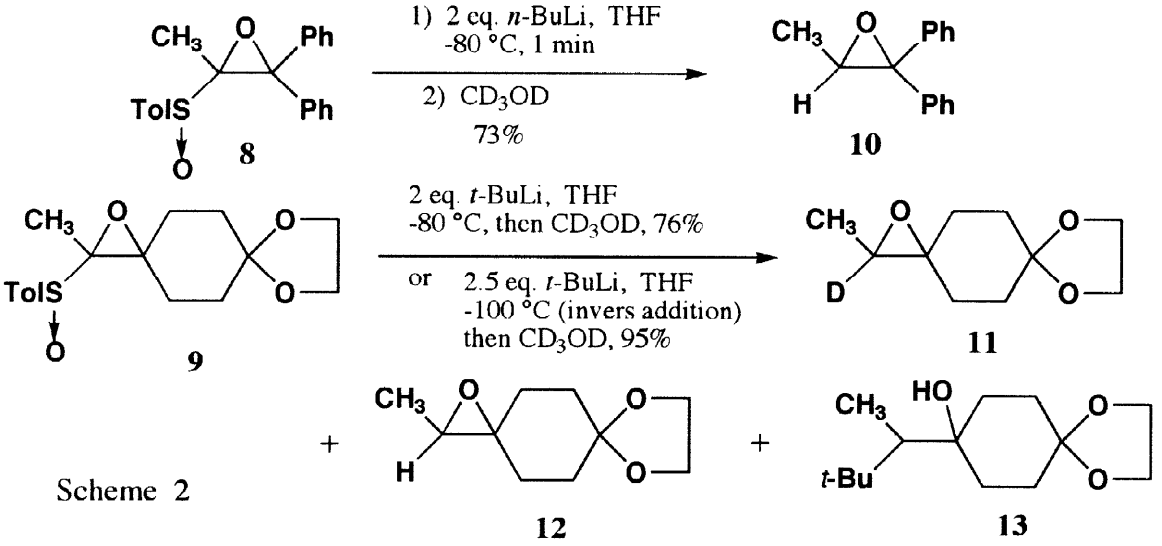
This reaction as shown in Scheme 1 was quite likely to take place; however, it has not been proved yet. At the same time, we thought that, if the mechanism is correct, we could trap the generated oxiranyllithium **4** with electrophiles when *t*-BuLi reacts with the sulfinyloxirane **3**. Because the produced aryl *tert*-butyl sulfoxide **6** does not have any acidic hydrogen, the generated oxiranyllithium **4** can be present for a few minitues at low temperature.

Generation of Oxiranyllithiums from Sulfinyloxiranes Having a Methyl Group via the Ligand Exchange Reaction of Sulfoxide with *t*-BuLi and the Properties of the Generated Oxiranyllithum.

To verify the above expectation, we first investigated the ligand exchange reaction of sulfoxides with alkyllithiums using sulfinyloxirans **8** and **9**[14] as the typical sulfinyloxirans (Scheme 2). First, 2 equivalents of *n*-BuLi was added to a solution of **8** in dry THF at -80 °C and after 1 min, the reaction was quenched with deuterated methanol (CD_3OD). This reaction cleanly gave desulfinylated epoxide **10** in good yield. Inspection of the ^1H NMR spectrum of the product showed that no deuterium was incorporated in the desulfinylated product **10**. The same treatment of **9** with *n*-BuLi followed by CD_3OD gave also the desulfinylated compound **12** having no deuterium.

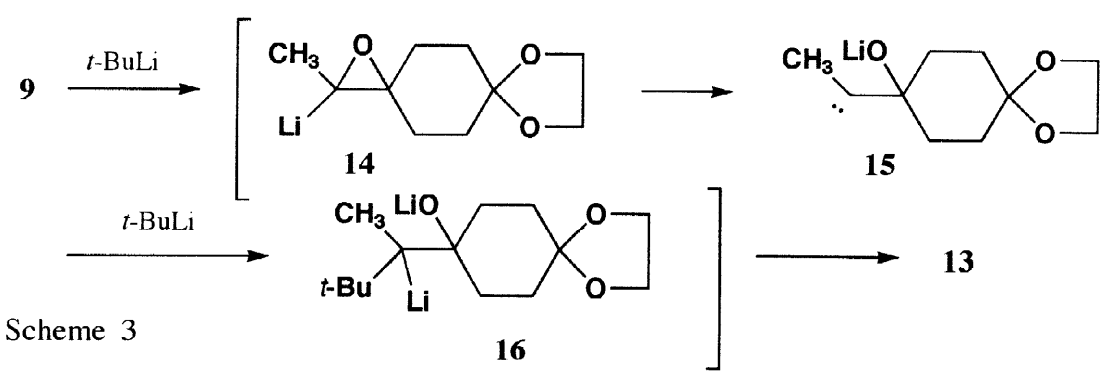
Next, two equivalents of *t*-BuLi was added to a solution of **9** in THF at -80 °C and after 30 sec, excess CD_3OD was added. Fortunately, this reaction cleanly gave desulfinylated epoxide in 76% yield. Inspection of the ^1H NMR spectrum showed, however, the product was an approximate 1:1 mixture of deuterated **11** and non-deuterated **12**.

This result showed us two important aspects of the nature of this ligand exchange reaction of the sulfinyloxirane. First, *t*-BuLi is as effective as *n*-BuLi in the ligand exchange reaction of sulfoxide, and the reaction is quite rapid even at very low temperature. Second, because the hydrogen on the oxirane carbon of **12** must come from a trace of moisture in THF, the rate of the ligand exchange reaction should be as fast as the protonation of *t*-BuLi.[15]



Scheme 2

To prevent this protonation, we modified the conditions of the ligand exchange reaction. Thus, 2.5 equiv. of *t*-BuLi was first added dropwise to THF at -100 °C. In this way the trace moisture in THF is removed. A solution of **9** in a minimum amount of THF was then added to the solution (inverse addition) and after 30 sec, the reaction was quenched with excess of CD_3OD. This treatment gave the desulfinylated epoxide **11** in 95% yield. ^1H NMR of the product showed that the deuterium content was 95%. This reaction also gave *tert*-butyl *p*-tolyl sulfoxide in 92% yield. From these experiments we were indeed able to generate the destabilized oxiranyllithium **14** (Scheme 3).



Scheme 3

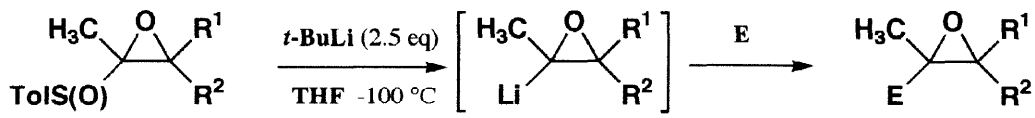
Careful inspection of the ^{1}H NMR showed the product was a mixture of **11**, **12**, and alcohol **13**. Several trials to isolate **13** were fruitless; however, the IR of the product showed 3509 cm^{-1} for the hydroxy group and ^{1}H NMR (δ 0.93 (d, J=7 Hz, CH_3) and 1.04 (s, $C(CH_3)_3$) of the product is consistent with the structure of **13**. From the ^{1}H NMR spectrum, the yield of **13** was found to be about 9%. The formation of **13** was thought to be as follows (Scheme 3). The oxiranyllithium decomposed to β-oxido carbenoid **15**, which was reacted with excess t-BuLi to afford dianion **16**. The dianion **16** was protonated to give **13**.[16]

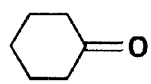
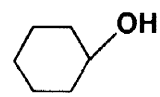
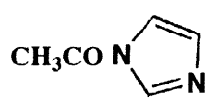
To investigate the stability of **14**, sulfinyloxirane **9** was treated with t-BuLi at -100 °C and after 15 min the reaction was quenched with CD_3OD. The reaction was still clean and the product was again a mixture of **11** and **13**; however, the yield of **13** was increased to about 30%. This result indicates that the oxiranyllithium **14** is unstable even at -100 °C.

Trapping the Generated Oxiranyllithiums with Several Electrophiles.

We next investigated the reactivities of the generated oxiranyllithiums with several electrophiles. The reaction was conducted as follows. Sulfinyloxirans **8** or **9** in a minimum amount of THF was added dropwise to a solution of t-BuLi (2.5 eq) in THF at -100 °C. After 30 sec, 2.7 equivalents of an electrophile was added and the reaction mixture was stirred at -100 °C for 10 to 30 min. The results are summarized in Table 1.

Table 1. Generation of Destabilized Oxiranyllithiums and Trapping Them with Electrophiles

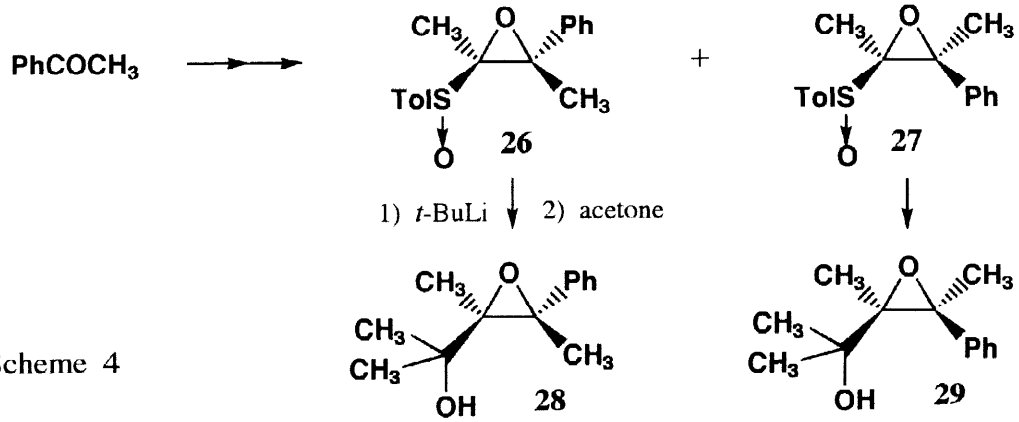


Entry	Sulfinyloxirane	Electrophile	Product (Yield/%)[a]
1	**8** R^1=R^2=Ph	CH_3CH_2CHO	**17** E=CH_3CH_2CHOH (80)
2			**18** E=  (83)
3		$(CH_3)_3SiCl$	**19** E= $(CH_3)_3Si$ (82)
4		EtOCOCl	**20** E= EtOCO (87)
5		Et_2NCOCl	**21** E= Et_2NCO (66)
6			**22** E= CH_3CO (28)
7	**9** R^1=R^2= $(CH_2)_2C(CH_2)_2$	PhCHO	**23** E= PhCHOH (86)
8		CH_3COCH_3	**24** E= $(CH_3)_2COH$ (82)
9		$(CH_3)_3SiCl$	**25** E= $(CH_3)_3Si$ (42)

a) Isolated purified yield after silica gel column chromatography.

As shown in the Table, the generated destabilized oxiranyllithiums were found to have enough reactivity toward several electrophiles. However, the yields varied with the electrophile used. Entries 1, 2, 7, and 8 showed that both aldehydes and ketones react equally well with the generated oxiranyllithiums. The yields of the silylation (entries 3 and 9) were found to vary with the oxiranyllithiums. Ethyl chloroformate was found to be the best electrophile giving the ethoxycarbonylated product in high yield (entry 4). Aminocarbonylation (entry 5) and acetylation (entry 6) were possible; however, the yields varied with the electrophiles.

It has already been reported that many kinds of oxiranyl anions are configurationally stable.[3] To ascertain whether the configuration of the oxiranyllithium generated by our method is stable or not, we carried out the following experiment (Scheme 4).



Scheme 4

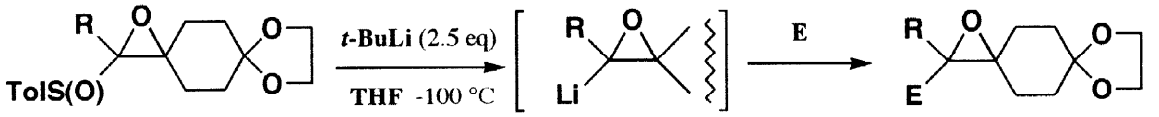
Diastereomers of sulfinyloxirans **26** and **27** were synthesized from acetophenone and the configuration was established by NOESY spectrum. The oxiranyllithiums of **26** and **27** were generated by the above-mentioned method and acetone was allowed to react with the anion. The reaction gave the adducts **28** and **29** in 81% and 74% yields, respectively, and it was found that the product was a single isomer. These results showed that the configuration of the oxiranyllithiums generated is stable under our conditions.

Generation of Oxiranyllithiums Having an Alkyl Group Other Than a Methyl Group and Investigation of Their Reactivity.

The above-mentioned method was applied to the sulfinyloxiranes having a more sterically hindered alkyl group (**30** and **31**) and the results are summarized in Table 2. Entries 1, 2, and 6 indicate that these sulfinyloxiranes also give the oxiranyllithium in high yields at -100 °C with *t*-BuLi. The oxiranyllithium reacted with ethyl chloroformate to give the products **34** and **37** (entries 3 and 7) in good yields.

Clear difference in the reactivity between the oxiranyllithiums generated from **8**, **9** (Table 1) and **30**, **31** (Table 2) was observed when the latter oxiranyllithiums were allowed to react with acetone and benzaldehyde. As mentioned above, oxiranyllithium having a methyl group reacted both with ketones (acetone and cyclohexanone) and aldehydes (propanal and benzaldehyde) in good yields (see Table 1). However, in the case of the oxiranyllithiums generated from sulfinyloxiranes having a bulky alkyl group (**30** and **31**), they gave only a trace (entry 4, Table 2) or very low yield (entry 8, Table 2) of the adduct with acetone. The main products were protonated epoxides **32** and **36**. Even with benzaldehyde the yields of the adduct were moderate (entries 5 and 9). These results imply that the phenethyl and the isopropyl groups hinder the reaction between the carbanion center and the carbonyl carbon and the oxiranyllithiums act as a base to abstract the acidic hydrogen on acetone.

Table 2. Generation of Destabilized Oxiranyllithiums from the Sulfinyloxiranes Having a Sterically Hindered Alkyl Group and Trapping Them with Electrophiles



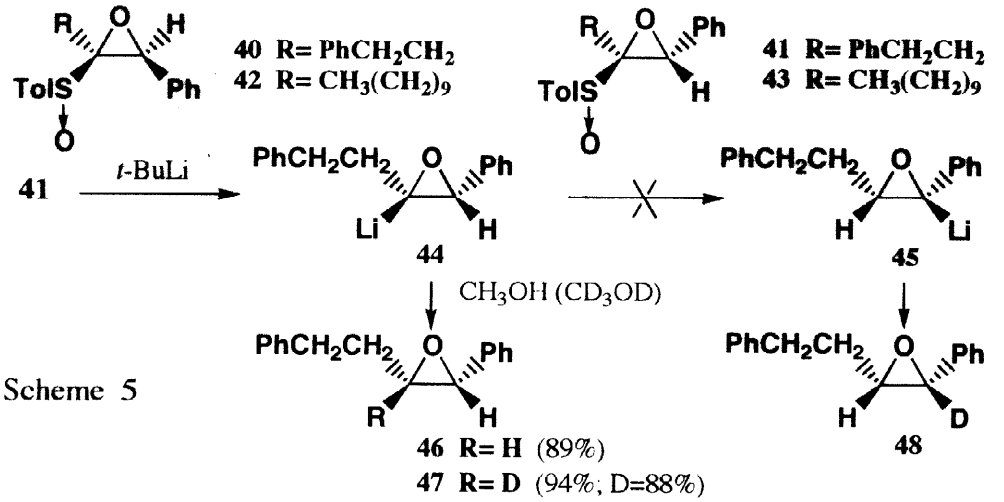
Entry	Sulfinyloxirane	Electrophile[a]		Product (Yield/%)[b]
1	**R= CH_2CH_2Ph**	**CH_3OH**	**32**	**E= H** (88)
2	**30**	**CD_3OD**	**33**	**E= D** (97; D=94%)
3		**EtOCOCl**	**34**	**E= EtOCO** (77)
4		**CH_3COCH_3**	**32**	**E= H** (72)
5		**PhCHO**	**35**	**E= PhCHOH** (44)
6	**R=$CH(CH_3)_2$**	**CH_3OH**	**36**	**E= H** (91)
7	**31**	**EtOCOCl**	**37**	**E= EtOCO** (85)
8		**CH_3COCH_3**	**38**	**E= $(CH_3)_2COH$** (20)
			36	**E= H** (73)
9		**PhCHO**	**39**	**E= PhCHOH** (62)

a) All the reactions were carried out as follows. A solution of the sulfinyloxirane (0.3 mmol) in a minimum amount of dry THF was added dropwise to a solution of *t*-BuLi (0.75 mmol) in THF (6 ml) at -100 °C. After 30 sec, the electrophile (0.8 mmol) was added and the reaction mixture was stirred at -100 °C for 10-30 min, then the reaction was quenched by adding aqueous NH_4Cl. b) Isolated purified yield after silica gel column chromatography.

Generation of Oxiranyllithiums Having a Phenyl Group at the β-Position.

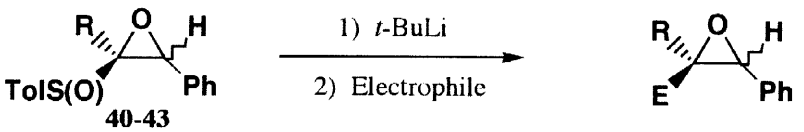
We investigated the above-mentioned reaction with the sulfinyloxiranes derived from benzaldehyde **40-43**. In these cases, we were interested in the reactivity of the oxiranyllithiums and also the feasibility of the reaction for the rearrangement of the carbanion (the rearrangement of carbanion **44** to **45**; Scheme 5).

Sulfinyloxirans **40-43** were easily synthesized from 1-chloro-3-phenylpropyl *p*-tolyl sulfoxide and 1-chloroundecyl *p*-tolyl sulfoxide, and benzaldehyde in almost quantitative yields and the configurations of the sulfinyloxirans were easily determined by ^1H NMR. First, **41** was treated with *t*-BuLi followed by methanol to give **46** in 89% yield. The value of the coupling constant of the hydrogen on the carbon bearing a phenyl group (δ 4.07, *J*=4.5 Hz) revealed that the configuration of **46** is *Z*. This fact again showed that the configuration of the oxiranyllithium **44** is quite stable. Next, the oxiranyllithium **44** was reacted with deuterated methanol to afford deutrated epoxide in 94% yield. Detailed inspection of the ^1H NMR of the product showed that the



Scheme 5

Table 3. Generation of Destabilized Oxiranyllithiums from the Sulfinyloxiranes Having a Phenyl Group **40-43** and Trapping Them with Electrophiles



Entry	Sulfinyloxirane	Electrophile[a]		Product (Yield/%)[b]
1	**40**	CH_3OH	**49**	**E= H** (99)
2	**41**	CH_3OH	**46**	**E= H** (89)
3	**40**	CD_3OD	**50**	**E= D** (75; D=84%)
4	**41**	CD_3OD	**47**	**E= D** (94; D=88%)
5	**40**	EtOCOCl	**51**	**E= EtOCO** (75)
6	**41**	EtOCOCl	**52**	**E= EtOCO** (50)
7	**42**	CH_3OH	**53**	**E= H** (99)
8	**43**	CH_3OH	**54**	**E= H** (87)
9	**42**	CD_3OD	**55**	**E= D** (99; D=91%)
10	**43**	CD_3OD	**56**	**E= D** (99; D=82%)
11	**42**	EtOCOCl	**57**	**E= EtOCO** (80)
12	**43**	EtOCOCl	**58**	**E= EtOCO** (65)
13	**42**	PhCHO	**59**	**E= PhCH(OH)** (82)
14	**43**	PhCHO	**60**	**E= PhCH(OH)** (71)

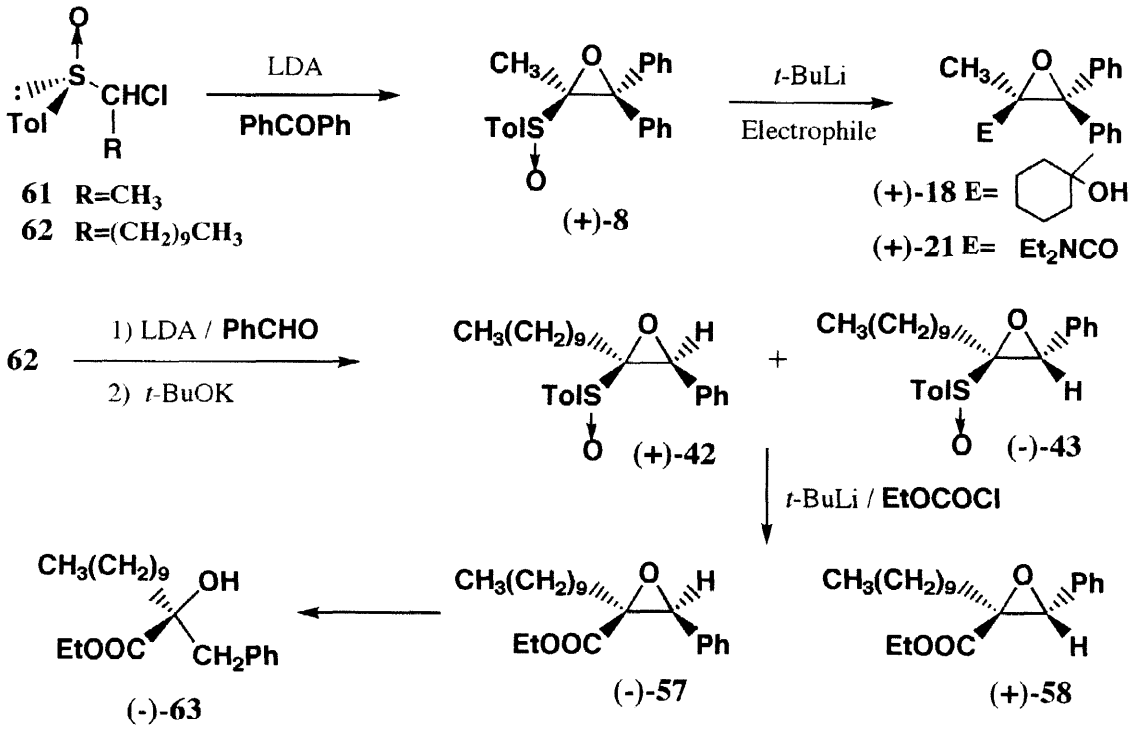
a) All the reactions were carried out as follows. A solution of the sulfinyloxirane (0.3 mmol) in a minimum amount of dry THF was added dropwise to a solution of *t*-BuLi (0.75 mmol) in THF (6 ml) at -100 °C. After 30 sec, the electrophile (0.8 mmol) was added and the reaction mixture was stirred at -100 °C for 10-30 min, then the reaction was quenched by adding aqueous NH_4Cl. b) Isolated purified yield after silica gel column chromatography.

product is **47** and no isomer **48** was observed. This result clearly showed that the generated carbanion did not rearrange even though the hydrogen on the carbon bearing the phenyl group is more acidic than that on the carbon bearing the phenethyl group.

The results for generation of the oxiranyllithiums from the sulfinyloxirans **40-43** and trapping them with several electrophiles are summarized in Table 3. Generally speaking, both the *E*- and *Z*-isomers showed no significant difference in reactivity toward electrophiles; however, the *Z*-isomer (**40** and **42**) tends to give slightly higher yields than the *E*-isomer (**41** and **43**) when reacted with ethyl chloroformate and benzaldehyde. Both oxiranyllithiums derived from **42** and **43** gave no adduct with acetone.

Asymmetric Synthesis of Tetrasubstituted Epoxides and α-Hydroxycarboxylic Ester.

We previously reported an asymmetric synthesis of di- and tri-substituted epoxides from optically active 1-chloroalkyl *p*-tolyl sulfoxides via the reductive desulfinylation of the sulfinyloxiranes with *n*-BuLi.[13d,e] In elaboration of the procedure mentioned above, we investigated the synthesis of optically active tetra-substituted epoxides and α-hydroxycarboxylic ester as shown in Scheme 6.



Scheme 6

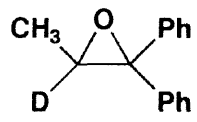
Optically pure sulfinyloxirane (+)-**8** was synthesized from optically pure (-)-1-chloroethyl *p*-tolyl sulfoxide **61** (prepared by methylation of optically pure (-)-chloromethyl *p*-tolyl sulfoxide[13e] with LDA and iodomethane) and benzophenone in quantitative yield. The oxiranyllithium generated from (+)-**8** was trapped with cyclohexanone and diethylcarbamoyl chloride to give (+)-**18** and (+)-**21**, respectively, in high yields. The optical purity was found to be over 98% by HPLC using a chiral column.[17]

Optically pure (-)-**62**[13e] was allowed to react with benzaldehyde followed by treatment with a base to afford optically active sulfinyloxiranes (+)-**42** and (-)-**43**. These were transformed to epoxides (-)-**57** and (+)-**58** by

the method described above. Catalytic hydrogenation of both (-)-**57** and (+)-**58** in ethanol with Pd-C gave the same α-hydroxycarboxylic ester (-)-**63** in quantitative yield. Optical purity was measured by HPLC using a chiral column.[17]

Generation of Oxiranylmagnesiums from Sulfinyloxiranes with EtMgCl and Their Properties.

Finally, we investigated the feasibility of the method for generation of oxiranylmagnesiums by the reaction of the sulfinyloxiranes with a Grignard reagent. Treatment of sulfinyloxirane **9** with 2 equivalents of EtMgCl in THF at -80 °C for 5 min gave over 70% of the recovered starting material **9** with some decomposition products and a trace of the desired **12** was observed on TLC. In contrast to this, treatment of **8** with 2 equivalents of EtMgCl at -80 °C for 1 min followed by CD_3OD afforded the desulfinylated and deuterated epoxide **64** in 70% yield with 95% D-content. The yield of **64** was improved to 85% when a solution of **8** was added to a solution of EtMgCl (2.5 equivalents) in THF at -100 °C for 3 min. This treatment also gave improved D-content (98%). At this stage, we were indeed able to generate the first example of oxiranyl Grignard reagent **65**.



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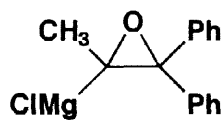

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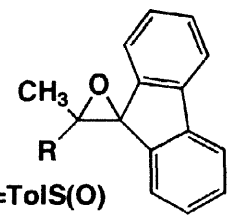
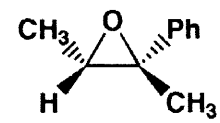


66 R=TolS(O)
67 R=H



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The oxiranylmagnesium **65** was found to be unstable like the oxiranyllithiums. For example, treatment of **8** with 2 equivalents of EtMgCl at -80 °C for 30 min followed by CD_3OD gave **64** in only 42% yield with some unknown by-products. Oxiranylmagnesium **65** was found to be quite unreactive with several electrophiles (benzaldehyde, acetone, cyclohexanone, ethyl chloroformate etc.) compared with the corresponding oxiranyllithium. For example, **65** did not react at all even with propionaldehyde.

We investigated the generation of the oxiranylmagnesiums with the sulfinyloxirane **66** derived from 9-fluorenone and the previously mentioned **26** and **27**. Sulfinyloxirane **66** was treated with EtMgCl at -80 °C for 1 min to give desulfinylated epoxide **67** in 51% yield. In this case, all the starting material **66** was consumed. The reaction of **26** and **27** (see Scheme 4) is interesting. Treatment of **26** with 2.5 equivalents of EtMgCl at -80 °C for 5 min gave **68** in 67% yield with no starting material. In contrast to this, the same treatment of **27** gave a trace of the desulfinylated product with about 70% recovery of the starting material. At any rate, from these results, it was found that the sulfinyloxiranes having at least one aromatic substituent on their β-position gave oxiranylmagnesium on treatment with EtMgCl. However, the rate of the ligand exchange reaction of sulfoxide with EtMgCl hangs on a delicate balance of the structure of the sulfinyloxiranes.

Experimental Section

All melting points are uncorrected. ^1H NMR spectra were measured in a $CDCl_3$ solution with JEOL GX-270 or GSX-500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silical gel FL-100D (Fuji-Silicia) containing 0.5% fluorescence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry reagent and solvent, diisopropylamine was distilled from CaH_2 and THF was

distilled from diphenylketyl. All the reagents are commercially available and purified by recrystallization or distillation before use. Methanol and liquid N_2 were used for the cooling bath at -100 °C.

1,2-Epoxy-1,1-diphenyl-2-(*p*-tolylsulfinyl)propane (8). Sulfinyloxirane **8** was synthesized from 1-chloroethyl *p*-tolyl sulfoxide and benzophenone as described in lit. 13e in 91% yield. Colorless prisms; mp 131-134 °C ($CHCl_3$-hexane); IR (KBr) 1045 (SO) cm^{-1}; ^1H NMR δ 1.20 (3H, s), 2.41 (3H, s), 7.2-7.8 (14H, m). Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79; S, 9.20. Found: C, 75.69; H, 5.70; S, 9.41.

2''-Methyl-2''-(*p*-tolylsulfinyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (9). Colorless crystals; mp 140-142 °C (AcOEt-hexane); IR (KBr) 1109, 1049, 1033 cm^{-1}; ^1H NMR δ 1.34 (3H, s), 1.7-2.4 (8H, m), 2.42 (3H, s), 3.99 (4H, m), 7.33, 7.55 (each 2H, d, *J*=8 Hz). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88; S, 9.94. Found: C, 63.25; H, 6.76; S, 10.08

1,2-Epoxy-1,1-diphenylpropane (10). *n*-BuLi (0.6 mmol) was added to a solution of **8** (105 mg; 0.3 mmol) in 3 ml of dry THF at -80 °C with stirring. The reaction mixture was stirred for 1 min, then CD_3OD (0.2 ml) was added. The reaction mixture was stirred at -80 °C for 10 min and then sat. aq. NH_4Cl was added. The whole was extracted with ether-benzene and the organic layer was washed once with sat. aq. NH_4Cl, dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give **10** (46 mg; 73%) as a colorless oil. IR (neat) 1448, 700 cm^{-1}; ^1H NMR δ 1.18 (3H, d, *J*=5.3 Hz), 3.49 (1H, q, *J*=5.3 Hz), 7.2-7.5 (10H, m). MS *m/z* (%) 210 (M^+, 30), 209 (29), 165 (100). Calcd for $C_{15}H_{14}O$: M, 210.1043. Found: *m/z* 210.1027.

2''-Deuterio-2''-methyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (11). *t*-BuLi (0.75 mmol) was added to 6 ml of dry THF at -100 °C. To this solution was added a solution of **9** (97 mg; 0.3 mmol) in 0.5 ml of dry THF at -100 °C with stirring. After 30 sec, CD_3OD (0.2 ml) was added. The workup described above gave 53 mg (95%) of **11** (containing about 9% of **13**) as a colorless oil and *tert*-butyl *p*-tolyl sulfoxide (54 mg; 92%). **11**: IR (neat) 1440, 1142, 1105, 1034 cm^{-1}; ^1H NMR δ 1.30 (3H, s), 1.5-2.0 (8H, m), 3.97 (4H, m). MS *m/z* (%) 185 (M^+, 2), 170 (18), 156 (43), 99 (100). Calcd for $C_{10}H_{15}DO_3$: M, 185.1161. Found: *m/z* 185.1162.

2''-Methyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (12). Treatment of **9** with *n*-BuLi followed by CD_3OD as described for the synthesis of **10** gave **12** as a colorless oil. IR (neat) 1440, 1124, 1099, 1036 cm^{-1}; ^1H NMR δ 1.30 (3H, d, *J*=5.5 Hz), 1.5-2.0 (8H, m), 2.92 (1H, q, *J*=5.5 Hz), 3.97 (4H, m). MS *m/z* (%) 184 (M^+, 2), 169 (15), 155 (51), 99 (85), 86 (100). Calcd for $C_{10}H_{16}O_3$: M, 184.1098. Found: *m/z* 184.1101.

1,2-Epoxy-3-hydroxy-2-methyl-1,1-diphenylpentane (17). *t*-BuLi (0.5 mmol) was added dropwise to 4 ml of dry THF at -100 °C. To this solution was added a solution of **8** (70 mg; 0.2 mmol) in 0.8 ml of THF dropwise with stirring. After 30 sec, propionaldehyde (0.6 mmol) was added and the reaction mixture was stirred at -100 °C for 15 min. The reaction was quenched by adding sat. aq. NH_4Cl. The whole was extracted with ether-benzene. The organic layer was washed once with sat. aq. NH_4Cl and dried over $MgSO_4$. The product was purified by silica gel column chromatography to afford **17** (43 mg; 80%) as a colorless oil (about 2:1 diastereomeric mixture). IR (neat) 3458 (OH), 1448, 706 cm^{-1}; ^1H NMR δ 0.81 (2H, t, *J*=7.3 Hz), 0.92 (1H, t, *J*=7.3 Hz), 1.17 (1H, s), 1.18 (2H, s), 1.5-1.8 (2H, m), 3.05 (1H, m), 7.2-7.6 (10H, m). MS *m/z* (%) 268 (M^+, 0.4), 250 ($[M-H_2O]^+$, 0.9), 221 (40), 165 (100). Calcd for $C_{18}H_{20}O_2$: M, 268.1461. Found: *m/z* 268.1453.

1,2-Epoxy-2-(1-hydroxycyclohexyl)-1,1-diphenylpropane (18). Above-mentioned reaction was carried out with cyclohexanone to give **18** as a colorless oil in 83% yield. IR (neat) 3572, 3504 (OH), 1448, 706 cm^{-1}; ^1H NMR δ 1.16 (3H, s), 1.4-1.9 (10H, m), 7.1-7.6 (10H, m). MS *m/z* (%) 290 ($[M-H_2O]^+$, 11), 210 (27), 166 (100). Calcd for $C_{21}H_{22}O$ ($M-H_2O$): M, 290.1669. Found: *m/z* 290.1655.

1,2-Epoxy-2-trimethylsilyl-1,1-diphenylpropane (19). Colorless oil; IR (neat) 1448, 1250, 839 cm^{-1}; ^1H NMR δ 0.02 (9H, s), 1.30 (3H, s), 7.3-7.8 (10H, m). MS *m/z* (%) 282 (M^+, 43), 267 (13), 208 (44), 165 (100). Calcd for $C_{18}H_{22}OSi$: M, 282.1438. Found: *m/z* 282.1438.

2-Ethoxycarbonyl-1,2-epoxy-1,1-diphenylpropane (20). Colorless oil; IR (neat) 1753, 1726 (CO), 1136 cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7.3 Hz), 1.43 (3H, s), 3.89 (2H, q, *J*=7.3 Hz), 7.1-7.6 (10H, m). MS *m/z* (%) 282 (M^+, 2), 281 (3), 253 (4), 236 (7), 208 (69), 165 (100). Calcd for $C_{18}H_{18}O_3$: M, 282.1255. Found: *m/z* 282.1272.

2-(*N*,*N*-Diethylaminocarbonyl)-1,2-epoxy-1,1-diphenylpropane (21). Colorless oil; IR (neat) 1635 (CO), 1448, 1381, 1074, 704 cm^{-1}; ^1H NMR δ 0.65 (6H, t, *J*=6.9 Hz), 1.42 (3H, s), 3.54 (4H, m), 7.1-7.6 (10H, m). MS *m/z* (%) 309 (M^+, 60), 165 (100). Calcd for $C_{20}H_{23}NO_2$: M, 309.1728. Found: *m/z* 309.1747.

2-Acetyl-1,2-epoxy-1,1-diphenylpropane (22). Colorless oil; IR (neat) 1709 (CO) cm^{-1}; ^1H NMR δ 1.32 (3H, s), 1.71 (3H, s), 7.2-7.5 (10H, m). MS *m/z* (%) 252 (M^+, 6), 209 (39), 165 (100). Calcd for $C_{17}H_{16}O_2$: M, 252.1148. Found: *m/z* 252.1134.

2''-[Hydroxy(phenyl)methyl]-2''-methyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (23). About 2:1 diastereomeric mixture; colorless oil; IR (neat) 3452 (OH), 1142, 1099, 1038 cm^{-1}; ^1H NMR δ 1.18 (1H, s), 1.20 (2H, s), 1.6-2.2 (8H, m), 3.99 (4H, m), 4.85 (1H, bs), 7.2-7.5 (5H, m). MS *m/z* (%) 290 (M^+, 0.1), 272 ($[M-H_2O]^+$, 0.8), 184 (24), 134 (77), 122 (83), 99 (100). Calcd for $C_{17}H_{22}O_4$; M, 290.1516. Found: *m/z* 290.1500.

2''-(1-Hydroxy-1-methylethyl)-2''-methyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (24). Colorless oil; IR (neat) 3485 (OH), 1144, 1097 cm^{-1}; ^1H NMR δ 1.28, 1.31, 1.34 (each 3H, s), 1.7-2.6 (8H, m), 3.97 (4H, m). MS *m/z* (%) 227 ([M-CH_3]$^+$, 1.6), 183 (82), 99 (98), 86 (100). Calcd for $C_{12}H_{19}O_4$ (M-CH_3): M, 227.1282. Found: *m/z* 227.1283.

2''-Methyl-2''-trimethylsilyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (25). Colorless oil; IR (neat) 1252, 1097, 841 cm^{-1}; ^1H NMR δ 0.14 (9H, s), 1.27 (3H, s), 1.5-1.8 (8H, m), 3.98 (4H, m). MS *m/z* (%) 256 (M$^+$, 7), 241 (46), 227 (35), 195 (51), 155 (89), 73 (100). Calcd for $C_{13}H_{24}O_3Si$: M, 256.1493. Found: *m/z* 256.1503.

(*E*)-2,3-Epoxy-2-phenyl-3-(*p*-tolylsulfinyl)butane (26) and (*Z*)-Isomer (27). These sulfinyloxiranes were synthesized from acetophenone and 1-chloroethyl *p*-tolyl sulfoxide. **26**: Colorless needles; mp 82-84 °C (AcOEt-hexane); IR (KBr) 1448, 1099, 1080, 1047 (SO) cm^{-1}; ^1H NMR δ 0.99, 2.11, 2.43 (each 3H, s), 7.2-7.7 (9H, m). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.19. Found: C, 71.05; H, 6.24; S, 11.41.

27: Colorless prisms; mp 101-102 °C (AcOEt-hexane); IR (KBr) 1491, 1078, 1049 (SO) cm^{-1}; ^1H NMR δ 1.46, 1.73, 2.41 (each 3H, s), 7.2-7.6 (9H, m). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.19. Found: C, 71.22; H, 6.27; S, 11.41.

(*E*)-3,4-Epoxy-2,3-dimethyl-4-phenyl-2-pentanol (28) and (Z)-Isomer (29). **28**: Colorless crystals; mp 107-108 °C (hexane); IR (KBr) 3483 (OH), 1371 cm^{-1}; ^1H NMR δ 0.90, 1.38, 1.43, 1.90 (each 3H, s), 7.2-7.4 (5H, m). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.77; H, 8.75. **29**: Colorless crystals; mp 65-57 °C (hexane); IR (KBr) 3504 (OH), 1138 cm^{-1}; ^1H NMR δ 1.08, 1.26, 1.51, 1.59 (each 3H, s), 7.2-7.4 (5H, m). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.97; H, 8.81.

2''-(2-Phenylethyl)-2''-(*p*-tolylsulfinyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (30). Colorless crystals; mp 107-109 °C (AcOEt-hexane); IR (KBr) 1452, 1143, 1099, 1042 cm^{-1}; ^1H NMR δ 1.6-2.6 (12H, m), 2.43 (3H, s), 4.00 (4H, m), 6.8-7.3 (5H, m), 7.37, 7.64 (each 2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{24}H_{28}O_4S$: C, 69.87; H, 6.84; S, 7.77. Found: C, 69.81; H, 6.74; S, 8.03.

2''-Isopropyl-2''-(*p*-tolylsulfinyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (31). Colorless crystals; mp 118-119 °C (AcOEt-hexane); IR (KBr) 1081, 1046 cm^{-1}; ^1H NMR δ 0.59, 1.15 (each 3H, d, *J*=7.2 Hz), 1.7-2.5 (8H, m), 2.41 (3H, s), 2.69 (1H, m), 4.00 (4H, m), 7.31, 7.56 (each 2H, d, *J*=8.1 H). Anal Calcd for $C_{19}H_{26}O_4S$: C, 65.11; H, 7.48; S, 9.15. Found: C, 64.98; H, 7.33; S, 9.15.

2''-(2-Phenylethyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (32). Colorless oil; IR (neat) 1454, 1098, 911 cm^{-1}; ^1H NMR δ 1.5-2.0 (10H, m), 2.7-2.9 (2H, m), 2.83 (1H, t, *J*=6.2 Hz), 3.95 (4H, m), 7.2-7.4 (5H, m). MS *m/z* (%) 274 (M$^+$, 7), 245 (38), 118 (49), 99 (70), 86 (100). Calcd for $C_{17}H_{22}O_3$: M, 274.1568. Found: *m/z* 274.1573.

2''-Deuterio-2''-(2-phenylethyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (33). Colorless oil; IR (neat) 1454, 1099, 914 cm^{-1}; ^1H NMR: the signal of the hydrogen on the epoxide ring (δ 2.83) of **32** almost disappeared. MS *m/z* (%) 275 (M$^+$, 7), 246 (45), 119 (45), 99 (100), 86 (93). Calcd for $C_{17}H_{21}DO_3$: M, 275.1631. Found: *m/z* 275.1640.

2''-Ethoxycarbonyl-2''-(2-phenylethyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (34). Colorless oil; IR (neat) 1747, 1723 (CO), 1454, 1176, 1091 cm^{-1}; ^1H NMR δ 1.29 (3H, t, *J*=7.1 Hz), 1.6-1.9 (9H, m), 2.53 (1H, m), 2.70 (1H, m), 2.87 (1H, m), 3.96 (4H, m), 4.21 (2H, m), 7.17-7.31 (5H, m). MS *m/z* (%) 346 (M$^+$, 3), 317 (17), 273 (39), 242 (35), 99 (100). Calcd for $C_{20}H_{26}O_5$: M, 346.1778. Found: *m/z* 346.1780.

2''-[Hydroxy(phenyl)methyl]-2''-(2-phenylethyl)dispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (35). Colorless oil (about 3:1 diastereomeric mixture); IR (neat) 3458 (OH), 1454, 1139, 1097, 1034 cm^{-1}; ^1H NMR δ 1.5-2.2 (10H, m), 2.74 (1H, m), 2.83 (2H, m), 3.95 (4H, m), 4.70 (3/4H, s), 4.93 (1/4H, s), 6.9-7.4 (10H, m). MS *m/z* (%) 362([M-H_2O]$^+$, trace), 274 (13), 245 (49), 86 (100).

2''-Isopropyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (36). Colorless oil; IR (neat) 1127, 1092 cm^{-1}; ^1H NMR δ 0.96 (3H, d, *J*=6.8 Hz), 1.08 (3H, d, *J*=6.8 Hz), 1.5-1.9 (9H, m), 2.47 (1H, d, *J*=9.4 Hz), 3.98 (4H, m). MS *m/z* (%) 212 (M$^+$, 2), 197 (3), 183 (66), 99 (65), 86 (100). Calcd for $C_{12}H_{20}O_3$: M, 212.1410. Found: *m/z* 212.1397.

2''-Ethoxycarbonyl-2''-isopropyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (37). Colorless oil; IR (neat) 1746, 1728 (CO), 1283, 1143, 1094, 1035 cm^{-1}; ^1H NMR δ 1.05 (3H, d, *J*=6.7 Hz), 1.15 (3H, d, *J*=7.3 Hz), 1.03 (3H, t, *J*=7 Hz), 1.7-2.1 (9H, m), 3.97 (4H, m), 4.25 (2H, m). MS *m/z* (%) 284 (M$^+$, 6), 255 (88), 209 (83), 185 (72), 99 (100). Calcd for $C_{15}H_{24}O_5$: M, 284.1623. Found: *m/z* 284.1633.

2''-(1-Hydroxy-1-methylethyl)-2''-isopropyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (38). Colorless crystals; mp 96-97 °C (AcOEt-hexane); IR (KBr) 3480 (OH), 1081 cm^{-1}; ^1H NMR δ 0.98 (3H, d, *J*=7.3 Hz), 1.11 (3H, d, *J*=7.3 Hz), 1.30 (3H, s), 1.37 (3H, s), 1.5-2.2 (8H, m), 3.97 (4H, m). MS *m/z* (%) 255 ([M-CH_3]$^+$, 1), 211 (48), 114 (100). Calcd for $C_{14}H_{23}O_4$ (M-CH_3): M, 255.1596. Found: *m/z* 255.1602.

2''-[Hydroxy(phenyl)methyl]-2''-isopropyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (39). Colorless oil; IR (neat) 3462 (OH), 1084 cm^{-1}; ^1H NMR δ 0.73 (3H, d, *J*=7.1 Hz),

0.85 (3H, d, *J*=7.4 Hz), 1.7-2.4 (9H, m), 4.00 (4H, s), 5.04 (1H, s), 7.25-7.40 (5H, m). MS *m/z* (%) 300 ([M-H_2O]$^+$, 10), 212 (33), 150 (100). Calcd for $C_{18}H_{23}O_4$ (M-H_2O): M, 300.1596. Found: *m/z* 300.1602.

(*Z*)-1,2-Epoxy-1,4-diphenyl-2-(*p*-tolylsulfinyl)butane (40) and (*E*)-Isomer (41). **40**: Colorless crystals; mp 128-130 °C (AcOEt-hexane); IR (KBr) 1452, 1042 (SO) cm^{-1}; ^{1}H NMR (90 MHz) δ 2.43 (3H, s), 2.5-2.9 (4H, m), 4.34 (1H, s), 7.0-7.7 (14H, m). Anal. Calcd for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12; S, 8.85. Found: C, 76.09; H, 5.99; S, 9.02. **41**: Colorless crystals; mp 98-101 °C (AcOEt-hexane); IR (KBr) 1450, 1055 (SO) cm^{-1}; ^{1}H NMR (90 MHz) δ 1.2-2.8 (4H, m), 2.44 (3H, s), 4.85 (1H, s), 6.8-7.8 (14H, m). Anal. Calcd for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12; S, 8.85. Found: C, 75.24; H, 5.95; S, 9.20.

(*Z*)-1,2-Epoxy-1-phenyl-2-(*p*-tolylsulfinyl)dodecane (42) and (*E*)-Isomer (43). **42**: Colorless crystals; mp 43.5-45.5 °C (hexane); IR (KBr) 1042 (SO), 807, 750, 698 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.1-1.4 (16H, m), 1.53 (1H, m), 2.30 (1H, m), 2.43 (3H, s), 4.42 (1H, s), 7.3-7.6 (9H, m). MS *m/z* (%) 398 (M$^+$, 2), 382 (6), 259 (13), 91 (100). Calcd for $C_{25}H_{34}O_2S$: M, 398.2280. Found: *m/z* 398.2277. **43**: Colorless crystals; mp 68-70.5 °C (hexane); IR (KBr) 1086, 1057 (SO), 811, 750, 707 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.0-1.5 (17H, m), 1.5-1.6 (1H, m), 2.44 (3H, s), 4.80 (1H, s), 7.2-7.7 (9H, m). MS *m/z* (%) 398 (M$^+$, 8), 382 (5), 259 (23), 91 (100). Calcd for $C_{25}H_{34}O_2S$: M, 398.2280. Found: *m/z* 398.2282.

(*Z*)-1,2-Epoxy-1,4-diphenylbutane (46). Colorless oil; IR (neat) 1496, 1454, 742, 699 cm^{-1}; ^{1}H NMR δ 1.57, 1.72, 2.62, 2.73 (each 1H, m), 3.24 (1H, m), 4.07 (1H, d, *J*=4.5 Hz), 7.0-7.4 (10H, m). MS *m/z* (%) 224 (M$^+$, 1), 133 (93), 118 (100). Calcd for $C_{16}H_{16}O$: M, 224.1199. Found: *m/z* 224.1200.

(*Z*)-1,2-Epoxy-2-deuterio-1,4-diphenylbutane (47). Colorless oil; IR (neat) 1496, 1454, 751, 699 cm^{-1}; ^{1}H NMR δ 1.57, 1.72, 2.62, 2.73 (each 1H, m), 4.07 (1H, s), 7.0-7.4 (10H, m). MS *m/z* (%) 225 (M$^+$, 0.5), 134 (76), 119 (100). Calcd for $C_{16}H_{15}DO$: M, 225.1262. Found: *m/z* 225.1255.

(*E*)-1,2-Epoxy-1,4-diphenylbutane (49). Colorless oil; IR (neat) 1496, 1455, 697 cm^{-1}; ^{1}H NMR δ 1.9-2.1 (2H, m), 2.77 (1H, m), 2.87 (1H, m), 2.96 (1H, m), 3.54 (1H, d, *J*=2.1 Hz), 7.1-7.4 (10H, m). MS *m/z* (%) 224 (M$^+$, 1), 133 (94), 118 (100). Calcd for $C_{16}H_{16}O$: M, 224.1199. Found: *m/z* 224.1199.

(*E*)-1,2-Epoxy-2-deuterio-1,4-diphenylbutane (50). Colorless oil; IR (neat) 1496, 1454, 746, 697 cm^{-1}; ^{1}H NMR δ 1.9-2.1 (2H, m), 2.77 (1H, m), 2.87 (1H, m), 3.54 (1H, s), 7.1-7.4 (10H, m). MS *m/z* (%) 225 (M$^+$, 1), 134 (70), 119 (100). Calcd for $C_{16}H_{15}DO$: M, 225.1262. Found: *m/z* 225.1254.

(*Z*)-1,2-Epoxy-2-ethoxycarbonyl-1,4-diphenylbutane (51) and (*E*)-Isomer (52). **51**: Colorless oil; IR (neat) 1748, 1732 (CO), 1182, 747, 699 cm^{-1}; ^{1}H NMR δ 0.94 (3H, t, *J*=7 Hz), 2.03 (1H, m), 2.62 (1H, m), 2.7-3.0 (2H, m), 3.90 (2H, q, *J*=7 Hz), 4.01 (1H, s), 7.1-7.6 (10H, m). MS *m/z* (%) 296 (M$^+$, 2), 205 (16), 135 (100). Calcd for $C_{19}H_{20}O_3$: M, 296.1410. Found: *m/z* 296.1414. **52**: Colorless oil; IR (neat) 1732 (CO), 1185, 728, 699 cm^{-1}; ^{1}H NMR δ 1.32 (3H, t, *J*=7 Hz), 2.0-2.9 (4H, m), 4.24 (2H, m), 4.34 (1H, s), 6.9-7.6 (10H, m). MS *m/z* (%) 296 (M$^+$, 3), 205 (17), 135 (100). Calcd for $C_{19}H_{20}O_3$: M, 296.1410. Found: *m/z* 296.1402.

(*E*)-1,2-Epoxy-1-phenyldodecane (53) and (*Z*)-Isomer (54). **53**: Colorless oil; IR (neat) 1463, 670 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-1.8 (18H, m), 2.94 (1H, m), 3.60 (1H, d, *J*=1.5 Hz), 7.2-7.4 (5H, m). MS *m/z* (%) 260 (M$^+$, 7), 231 (4), 169 (15), 107 (100). Calcd for $C_{18}H_{28}O$: M, 260.2138. Found: *m/z* 260.2134. **54**: Colorless oil; IR (neat) 1456, 742, 699 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-1.6 (18H, m), 3.20 (1H, m), 4.07 (1H, d, *J*=4 Hz), 7.2-7.4 (5H, m). MS *m/z* (%) 260 (M$^+$, 5), 213 (2), 169 (15), 159 (18), 107 (100). Calcd for $C_{18}H_{28}O$: M, 260.2138. Found: *m/z* 260.2142.

(*E*)-1,2-Epoxy-2-deuterio-1-phenyldodecane (55) and (*Z*)-Isomer (56). **55**: Colorless oil; IR (neat) 1461, 746 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-1.8 (18H, m), 3.60 (1H, s), 7.2-7.4 (5H, m). MS *m/z* (%) 261 (M$^+$, 4), 134 (18), 107 (100). Calcd for $C_{18}H_{27}DO$: M, 261.2202. Found: *m/z* 261.2205. **56**: Colorless oil; IR (neat) 1458, 757 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-1.6 (18H, m), 4.07 (1H, s), 7.2-7.4 (5H, m). MS *m/z* (%) 261 (M$^+$, 4), 159 (25), 107 (100). Calcd for $C_{18}H_{27}DO$: M, 261.2201. Found: *m/z* 261.2205.

(*Z*)-1,2-Epoxy-2-ethoxycarbonyl-1-phenyldodecane (57) and (*E*)-Isomer (58). **57**: Colorless oil; IR (neat) 1754, 1732 (CO), 1243, 1176, 1143 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=6.9 Hz), 0.94 (3H, t, *J*=7.1 Hz), 1.2-1.7 (17H, m), 2.35 (1H, m), 3.95 (2H, m), 4.03 (1H, s), 7.2-7.4 (5H, m). MS *m/z* (%) 332 (M$^+$, 5), 135 (100). Calcd for $C_{21}H_{32}O_3$: M, 332.2350. Found: *m/z* 332.2352. **58**: Colorless oil; IR (neat) 1732 (CO), 1276, 699 cm^{-1}; ^{1}H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.1-1.3 (17H, m), 1.34 (3H, t, *J*=7.1 Hz), 1.87 (1H, m), 4.27 (1H, s), 4.29 (2H, m), 7.25-7.50 (5H, m). MS *m/z* (%) 332 (M$^+$, 7), 199 (8), 135 (100). Calcd for $C_{21}H_{32}O_3$: M, 332.2350. Found: m/z 332.2352.

(*Z*)-1,2-Epoxy-2-[hydroxy(phenyl)methyl]-1-phenyldodecane (59) and (*E*)-Isomer (60). **59**: Colorless oil; IR (neat) 3446 (OH) cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.0-1.4 (16H, m), 1.62, 1.80 (each 1H, m), 4.19 (1H, s), 4.50 (1H, s), 6.96 (2H, m),7.1-7.5 (8H, m). MS *m/z* (%) 366 (M$^+$, 5), 364 (6), 348 ([M-H_2O]$^+$, 65), 260 (100). Calcd for $C_{25}H_{34}O_2$: M, 366.2559. Found: *m/z* 366.2567. **60**: Colorless oil (about 2:1 diastereomeric mixture); IR (neat) 3448 (OH) cm^{-1}; ^{1}H NMR δ 0.85 (3H, m), 1.0-1.5 (18H, m), 4.42 (1/3H,s), 4.54 (2/3H s), 4.85 (1/3H, s), 5.02 (2/3H, s), 7.2-7.6 (10H, m). MS *m/z* (%) 364 ([M-2]$^+$, 5.5), 260 (100).

(2*R*,*R*$_S$)-(+)-1,2-Epoxy-1,1-diphenyl-2-(*p*-tolylsulfinyl)propane (8). A solution of (-)-1-chloroethyl *p*-tolyl sulfoxide (1.0 g; 5 mmol) in 3 ml of THF was added to a solution of LDA (6.5 mmol) in 15 ml of THF at -70 °C dropwise with stirring. The stirring was continued at -70 °C for 10 min, and then a

solution of benzophenone (1.18 g; 6.5 mmol) in 3 ml of THF was added. The reaction mixture was stirred for 5 min, and then the reaction was quenched by adding sat. aq. NH_4Cl. The whole was extracted with ether-benzene and the organic layer was washed once with sat. aq. NH_4Cl, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (hexane:AcOEt=4:1) to give (+)-**8** (1.71g; 98%) as colorless crystals; mp 99-101 °C ($CHCl_3$-hexane); $[\alpha]_D^{25}$ +26.1° (*c* 0.13, acetone). Other spectral data see racemic **8**.

(*R*)-(+)-18. Colorless crystals; mp 78-79 °C (AcOEt-hexane). $[\alpha]_D^{25}$ +41.4° (*c* 0.2, acetone). Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.93; H, 7.76.

(*S*)-(+)-21. Colorless crystals; mp 108-109 °C (AcOEt-hexane); $[\alpha]_D^{25}$ +69.1° (*c* 0.2, acetone). Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.70; H, 7.42; N, 4.41.

(1*S*,2*R*,*R*$_S$)-42: $[\alpha]_D^{25}$ +16.1° (*c* 0.5, acetone). **(1*R*,2*R*,*R*$_S$)-43**: $[\alpha]_D^{25}$ -1.7° (*c* 0.4, acetone).

(1*S*,2*S*)-57: $[\alpha]_D^{25}$ -19.5° (*c* 0.6, acetone). **(1*R*,2*S*)-58**: $[\alpha]_D^{25}$ +1.0° (*c* 0.4, acetone).

(*S*)-(-)-Ethyl 2-benzyl-2-hydroxydodecanoate (63). To a solution of (-)-**57** (59 mg; 0.2 mmol) in 3 ml of EtOH was added 5 mg of Pd-C (10%) and the suspension was stirred in H_2 atmosphere at room temperature for 3 h. The Pd-C was filtered off and the solvent was evaporated to give a residue, which was purified by silica gel column chromatography (hexane:AcOEt=30:1) to give 58.5 mg (99%) of (-)-**63** as a colorless oil. $[\alpha]_D^{25}$ -12.6° (*c* 0.6, acetone). IR (neat) 3531 (OH), 1732 (CO), 1249, 1199 cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.05-1.65 (13H, m), 1.70 (1H, m), 1.87 (1H, m), 2.92, 3.02 (each 1H, d, *J*=13.4 Hz), 4.15 (2H, m), 7.1-7.3 (5H, m). MS *m/z* (%) 334 (M^+, 7), 316 (10), 261 (35), 169 (87), 92 (100). Calcd for $C_{21}H_{34}O_3$: M, 334.2506. Found: *m/z* 334.2520.

2-Deuterio-1,2-epoxy-1,1-diphenylpropane (64). Colorless oil; IR (neat) 1495, 1448, 700 cm^{-1}; ^1H NMR δ 1.17 (3H, s), 7.1-7.5 (10H, m). MS *m/z* (%) 211 (M^+, 28), 210 (30), 166 (63), 165 (100). Calcd for $C_{15}H_{13}DO$: M, 211.1106. Found: *m/z* 211.1108.

Sulfinyloxirane (66). Light yellow crystals; mp 109.5-111 °C (AcOEt-hexane); IR (KBr) 1448, 1084, 1049 (SO) cm^{-1}; ^1H NMR δ 1.66 (3H, s), 2.47 (3H, s), 7.1-7.9 (12H, m). MS *m/z* (%) 346 (M^+, 1), 287 (8), 246 (11), 208 (34), 165 (100). Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24; S, 9.26. Found: C, 75.64; H, 5.13; S, 9.30.

Epoxide (67). Colorless oil; IR (neat) 1448, 743 cm^{-1}; ^1H NMR δ 1.67 (3H, d, *J*=5.3 Hz), 3.84 (1H, q, *J*=5.3 Hz), 7.2-7.8 (8H, m). MS *m/z* (%) 208 (M^+, 62), 193 (9), 180 (24), 165 (86), 164 (100). Calcd for $C_{15}H_{12}O$: M, 208.0887. Found: *m/z* 208.0885.

(*Z*)-2,3-Epoxy-2-phenylbutane (68). Colorless oil; IR (neat) 1444, 1375, 764, 702 cm^{-1}; ^1H NMR δ 0.97 (3H, d, *J*=5.6 Hz), 1.64 (3H, s), 3.17 (1H, q, *J*=5.6 Hz), 7.2-7.5 (5H, m). MS *m/z* (%) 148 (M^+, 48), 147 (38), 105 (52), 104 (100).

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References and Notes

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14. The sulfinyloxiranes in this paper were synthesized from 1-chloroalkyl *p*-tolyl sulfoxides and corresponding ketones or aldehydes as described in a previous paper: Satoh, T.; Kumagawa, T.; Sugimoto, A.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 301. Experimental details, see also lit. 13b and 13e. Selected data are reported in experimental section.

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17. Daicel Chiralpak AD, 10% 2-propanol in hexane, flow rate 0.5 ml/min. The optical purity of (+)-**18**, (+)-**20**, and (-)-**63** were found to be over 98% ee.