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Acylations and Aldol-Type Reactions of Cyclopropyl α-Sulfonyl Carbanions

Rikuhei Tanikaga,* Shigeru Yamada, Takeshi Nishikawa, and Asako Matsui

Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University, Nojihigashi 1-1-1, Kusatsu, Shiga 525-8577, Japan

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Abstract: Acylations and aldol-type reactions of cyclopropyl α-sulfonyl carbanions formed from (1*R**,2*R**)-2-alkyl-1-(phenylsulfonyl)cyclopropanes (1*R**,2*R**)-**3** gave (1*R**,2*R**)-1-acyl-, and (1*R**,2*R**)-1-(1-hydroxyalkyl)-2-alkyl-1-(phenylsulfonyl)cyclopropanes [(1*R**,2*R**)-**6** and (1*R**,2*R**)-**8**] in high yields, respectively, but no diastereoisomeric (1*S**,2*R**)-products were formed. The carbanion generated from (1*S**,2*R**)-2-methyl-1-(phenylsulfonyl)cyclopropane (1*S**,2*R**)-**3b** led to rapid isomerization to provide a single diastereoisomeric (1*R**,2*R**)-product.

INTRODUCTION

An enantiomerically pure cyclopropane system is a common feature in a wide variety of natural products,[1] and a number of methods are available for its construction.[2] As an addition to the applications of sufur-based reagents to orgnic syntheses, recently we reported the synthesis of enantiomerically pure (1*R*,2*R*)- and (1*S*,2*S*)-2-alkyl-1-(phenylsulfonyl)cyclopropanes [(1*R*,2*R*)-**3** and (1*S*,2*S*)-**3**].[3] Since H-D exchage reaction of a carbanion generated from cyclopropane **3a** (R^1=H) was first investigated by Cram,[4] alkylations of cyclopropyl α-sulfonyl carbanions produced from **3b** (R^1=CH_3), 2-[2-(methoxy)ethoxy]methoxy-1-(phenylsulfonyl)cyclopropane, (1*R**,2*R**)-3,3-dimethyl-2-methoxy-1-(phenylsulfonyl)cyclopropane and 2,2-diphenoxy-1-(phenylsulfonyl)cyclopropane have been reported.[5-8] On the other hand, the X-ray structure determination of 2,2-diphenyl-1-(phenylsulfonyl)cyclopropyllithium was carried out by Boche.[9]

While the aldol-type reaction of **3a** with hexanal or acetone was reported,[5] there is no report on the general behavior in acylations and aldol-type reactions of 2-alkyl-1-(phenylsulfonyl)cyclopropanes **3**. Although 1-(phenylthio)cyclopropyllithium readily undergoes aldol-type reactions,[10,11] the carbanion of 1-(phenylthio)-cyclopropane containing a substituent at C-2 was found to be unstable.[10,12] The objective of this work is to elucidate the stereochemistry in acylations and aldol-type reactions of the carbanions generated from **3**.

RESULTS AND DISCUSSION

Although enantiomerically pure (1*R*,2*R*)-**3** and (1*S*,2*S*)-**3** were prepared using Baker's yeast,[3] racemic (1*R**,2*R**)-**3** were prepared with ease by the following way. Sulfides **1a** (Y=H) and **1b** (Y=CH_3) were obtained by 1,4-addition of benzenethiol to 2-propenal (acrolein) or 3-buten-2-one in quantitative yields, respectively. Treatment of **1b** with $NaBH_4$ in the customary manner gave alcohol **2b**, while reactions of **1a** with Grignard reagents R^1MgBr in general afforded alcohols **2**. According to the similar procedures as

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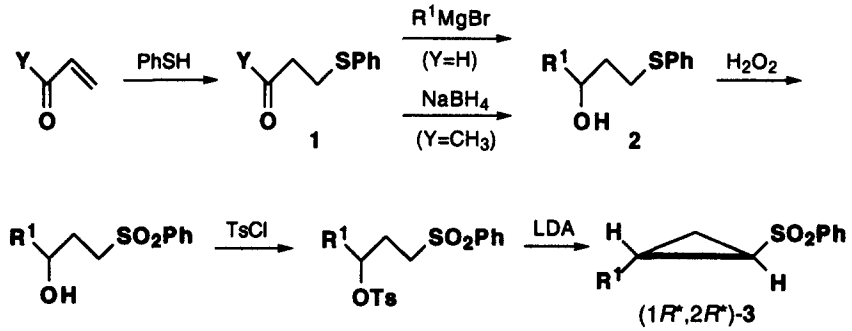
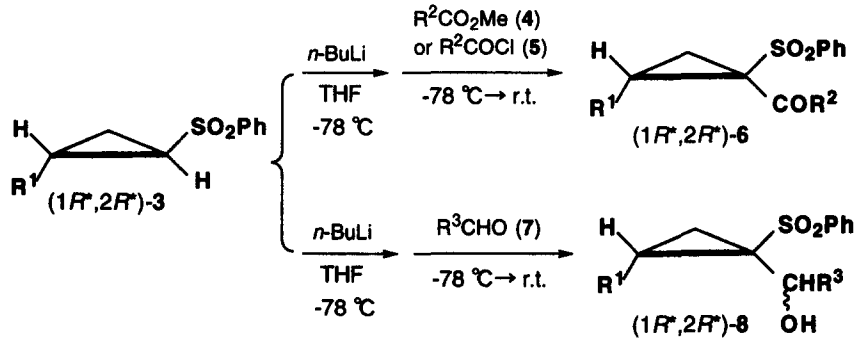
described in the literature,[5] (1*R**,2*R**)-**3** were synthesized efficiently as follows; (1) oxidation of **2** to sulfones, (2) tosylation, and (3) cyclopropanation with lithium diisopropylamide (LDA). In the present cyclization reaction the formation of diastereoisomeric (1*S**,2*R**)-**3** were not detected (Scheme 1).



Scheme 1

Upon treatment with methyl alkanoates **4** or acyl chlorides **5** the carbanions formed from (1*R**,2*R**)-**3** using *n*-BuLi in THF readily underwent acylation to provide acylcyclopropanes (1*R**,2*R**)-**6** in high yields, but not to afford diastereomeric (1*S**,2*R**)-isomers (Scheme 2).



Scheme 2

The stereochemistry of (1*R**,2*R**)-**6** was deduced by a combination of COSY and NOESY NMR spectra at 400 MHz. For example, in the spectrum of (1*R**,2*R**)-**6b** NOE was observed between CH_3 (2) and $CH_2CH_2CH_3$ located in *cis* configuration, and the absence of NOE between H (2) and $CH_2CH_2CH_3$ as shown in Fig. 1.

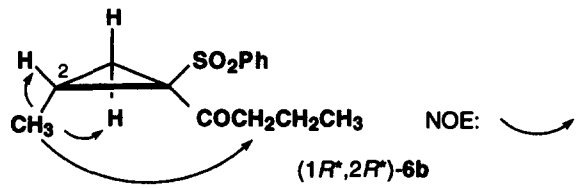


Fig. 1

These findings mean that the intermediary carbanion underwent C-C bond formation with retention of its configuration. The results obtained by these acylations are shown in Table 1.

Table 1. Preparation of Acylcyclopropanes (1*R**,2*R**)-**6**

R^1	**4** or **5**	R^2	product	yield (%)[a]
CH_3	**4a**	CH_3	**6a**	65
CH_3	**4b**	$CH_3(CH_2)_2$	**6b**	75
CH_3	**4c**	$(CH_3)_2CH$	**6c**	95
CH_3	**4d**	$CH_3(CH_2)_6$	**6d**	72
CH_3	**4e**	Ph	**6e**	92
$CH_3(CH_2)_2$	**4b**	$CH_3(CH_2)_2$	**6f**	63
Ph	**4b**	$CH_3(CH_2)_2$	**6g**	74
Ph	**4e**	Ph	**6h**	86
CH_3	**5b**	$CH_3(CH_2)_2$	**6b**	66
CH_3	**5c**	$(CH_3)_2CH$	**6c**	71
CH_3	**5d**	$CH_3(CH_2)_6$	**6d**	53

a Isolated yield.

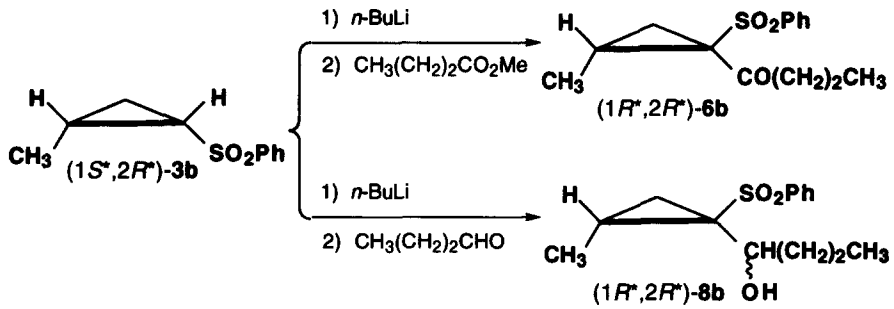
By a similar treatment of the anions of (1*R**,2*R**)-**3** with aldehydes **7**, the aldol-type reaction took place to afford a mixture of two diastereoisomeric (hydroxyalkyl)cyclopropanes **8**, and the analyses with HPLC revealed the absence of other diastereomeric isomers. The subsequent oxidation of the mixture of products **8** with pyridinium chlorochromate (PCC) yielded a single product (1*R**,2*R**)-**6**, and therefore, it was concluded that both diastereoisomeric products **8** have (1*R**,2*R**) configuration. These results are shown in Table 2.

Table 2. Aldol-Type Reactions of Cyclopropanes (1*R**,2*R**)-**3** with Aldehydes **7**

R^1	R^3	product	yield (%)[a]	diasteromeric ratio[b]
CH_3	$CH_3(CH_2)_2$	**8b**	87	55/45
CH_3	$(CH_3)_2CH$	**8c**	71	57/43
CH_3	$CH_3(CH_2)_6$	**8d**	86	69/31
CH_3	Ph	**8e**	96	57/43
$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	**8f**	74	58/42
Ph	$CH_3(CH_2)_2$	**8g**	74	55/45
Ph	Ph	**8h**	86	53/47

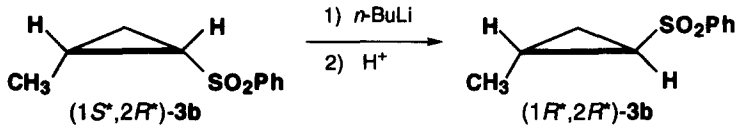
a Isolated yield. b Determined by HPLC.

Interestingly, the acylations and the aldol-type reactions starting from (1*S**,2*R**)-2-methyl-1-(phenylsulfonyl)cyclopropane (1*S**,2*R**)-**3b** gave the different results, that is, the configurations of products **6b** and **8b** were found to be (1*R**,2*R**), but not (1*S**,2*R**) (Scheme 3).



Scheme 3

These results suggest that the carbanion generated from (1*S**,2*R**)-**3** immediately underwent complete inversion of configuration to produce a thermodynamically stable product. The interconversion might be caused by the steric requirement of a bulky aggregation in which the sulfonyl group, the lithium cation, and THF molecules are held by chelation.[9,13,14] This assumption was confirmed by the experimental result that protonation of the carbanion generated from (1*S**,2*R**)-**3b** led to the formation of (1*R**,2*R**)-**3b** in a quantitative yield (Scheme 4).



Scheme 4

Since enantiomerically pure (1*R*,2*R*)- and (1*S*,2*S*)-2-alkyl-1-(phenylsulfonyl)cyclopropanes [(1*R*,2*R*)-**3** and (1*S*,2*S*)-**3**] have been synthesized[3] and a sulfonyl group may be converted into other functional groups,[15] the present preparative methods may be applicable to organic synthesis. In addition, these findings can also give some informations to the stereochemistry of a carbanion on a cyclopropane ring.

EXPERIMENTAL

NMR spectra were recorded with a JEOL JNM-A-400 (400 MHz) or a Bruker AC-300 (300 MHz) using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. IR spectra were taken on a Shimadzu FT-IR-8600 instrument. HPLC analyses were carried out with a Shimadzu LC-6A machine equipped with a Nacalai Tesque C_{18}-AR or a Nacalai Tesque PYE column. Column chromatography was performed with Wakogel 200 silica gel, and TLC with Merck silica gel 60 F_{254}. THF is freshly distilled from calcium hydride before use.

Preparations of 1-phenylthio-3-alkanols (2)

3-(Phenylthio)propanal (**1a**) and 1-phenylthio-3-butanone (**1b**) were readily prepared by 1,4-additions of benzenethiol to 2-propenal (acrolein) and 3-buten-2-one in quantitative yields, respectively. Treatment of **1b** with $NaBH_4$ in the customary manner gave 1-phenylthio-3-butanol (**2b**).

1-Phenylthio-3-hexanol **2c**. A Grignard reagent was prepared from 1-bromopropane (5.46 g, 60 mmol) and Mg (1.46 g, 60 mmol) in dry THF (30 ml) at room temperature under Ar in the customary manner and was cooled to 0 ℃. To the stirred solution was added a solution of **1a** (9.96 g, 60 mmol) in THF (20 ml) at 0 ℃ during a period of 1 h. The resultant solution was stirred for further 1 h after which the reaction was quenched with dilute hydrochloric acid and exracted with ethyl acetates (2 x 80 mL). The combined organic phase was washed with brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography [silica gel; eluent hexane-ethyl acetate (4:1)] gave **2c** (6.44 g, 51%) as a yellow liquid: IR (neat/cm^{-1}) ν_{max} 3361; ^{1}H NMR δ 0.88 (t, *J*=6.8 Hz, 3 H), 1.29-1.44 (m, 4 H), 1.84 (m, 2 H), 3.27 (m, 2 H), 3.68 (m, 1 H), 3.90 (br s, 1 H) and 7.28-8.04 (m, 5 H).

1-Phenylthio-3-phenyl-3-propanol **2d**. Upon the similar treatment of **1a** with a Grignard reagent prepared from bromobenzene and Mg the product **2d** was isolated as a colorless solid: yield 55%; mp 83 ℃; IR (Nujol/cm^{-1}) ν_{max} 3370; ^{1}H NMR δ 1.34 (m, 2 H), 3.27 (m, 2 H), 3.70 (m, 1 H), 3.98 (br s, 1 H) and 6.82-8.04 (m, 10 H).

Peparations of (1R,2R*)-2-alkyl-1-(phenylsulfonyl)cyclopropanes (1R*,2R*)-3*

According to the literature procedures for synthesis of enantiomerically pure (1*R*,2*R*)-2-methyl-1-(phenylsulfonyl)cyclopropanes (1*R*,2*R*)-**3b**,[3] racemic (1*R**,2*R**)-**3** were obtained from (1*R*,2*R*)-**2** as follows; (1) oxidation (H_2O_2-Na_2WO_4/methanol) to sulfones, (2) tosylation (*p*-toluenesulfonyl chloride/pyridine), and (3) cyclopropanation (LDA/THF).

The physical data of (1*R**,2*R**)-**3** are summarized below.

(1R,2R*)-2-propyl-1-(phenylsulfonyl)cyclopropanes (1R*,2R*)-3c*. Yield 55% (based on **2c**); a viscous liquid; IR (neat/cm^{-1}) ν_{max} 2928, 1448, 1306 and 1150; ^{1}H NMR δ 0.80-0.91 (m, 3 H), 1.11-1.27 (m, 5 H), 1.39 (m, 1 H), 1.68 (m, 1 H) , 2.19 (m, 1 H) and 7.52-7.92 (m, 5 H)(Found: C, 64.48; H, 7.03. Calcd. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19%).

(1R,2R*)-2-phenyl-1-(phenylsulfonyl)cyclopropanes (1R*,2R*)-3d*. Yield 57% (based on **2d**); a colorless solid; mp 89 ℃; IR (Nujol/cm^{-1}) ν_{max} 2930, 1448, 1307 and 1150; ^{1}H NMR δ 1.47 (ddd, *J*=5.0, 8.8, 6.1 Hz, 1 H), 1.89 (ddd, *J*=6.1, 5.0, 9.9 Hz, 1 H), 2.67 (ddd, *J*=8.8, 5.0, 6.0 Hz, 1 H), 2.89 (ddd, *J*=6.1, 9.9, 6.0 Hz, 1 H) and 7.00-7.95 (m, 5 H).

Preparation of (1S,2R*)-2-methyl-1-(phenylsulfonyl)cyclopropane (1S*,2R*)-3b*

The mixture of diastereoisomeric (1*S**,2*R**)-**3b** and (1*R**,2*R**)-**3b** was formed by an alternative method;[11] namely, cyclization of 2-methyl-1,3-di(phenylthio)propane **9**, followed by oxidation and then separation by column chromatography on silica gel: yield 10% (based on **9**); a viscous liquid; IR (neat/cm^{-1}) ν_{max} 2963, 1447, 1319 and 1148; ^{1}H NMR δ 1.27 (m, 1 H), 1.33 (m, 1 H), 1.41 (m, 1 H), 1.43 (d, *J*=1.2 Hz, 3 H) 2.41 (m, 1 H) and 7.54-7.94 (m, 5 H)(Found: C, 61.04; H, 5.99. Calcd. for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16%). [(1*R**,2*R**)-**3b**; yield 75% (based on **9**)].

Preparation of (1R,2R*)-1-acyl-2-alkyl-1-(phenylsulfonyl)cyclopropanes (1R*,2R*)- 6*

General procedure: To a stirred solution of **3b** (0.98 g, 5.0 mmol) in dry THF (30 mL) was added dropwise butyllithium (1.67 mol/L in hexane, 3.75 mL, 6.0 mmol) at -78 ℃ under Ar, and stirring was continued for 30 min at -78 ℃ after which ethyl acetate (0.53 g, 6 mmol) was added dropwise to the solution. The resultant solution was stirred at -80 ℃ for 30 min and then allowed to warm to room temperature over a period of 2 h before being treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate (2 x 50 mL), and the combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. HPLC analysis (column, C_{18}-AR or PYE; solvent, CH_3OH/H_2O=50/50; room temperature) of the residue revealed the formation of a single diastereoisomeric product. Column chromatography [silica gel, eluent

hexane-ethyl acetate (4:1)] gave (1*R**,2*R**)-1-acetyl-2-methyl-1-(phenylsulfonyl)cyclopropane (1*R**,2*R**)-**6a** (0.80 g, 65%) as a viscous liquid: IR (neat/cm^{-1}) ν_{max} 1702, 1448, 1307 and 1141; ^{1}H NMR δ 1.10 (d, *J*=6.3 Hz, 3 H), 1.60 (dd, *J*=7.8, 5.1 Hz, 1 H), 1.76 (dd, *J*=9.8, 5.1 Hz, 1 H), 2.41 (m, 1 H), 2.44 (s, 3 H) and 7.51-7.85 (m, 5 H). ^{1}H NMR spectrum of isolated (1*R**,2*R**)-**6a** exhibited the absence of (1*S**,2*R**)-isomer (Found: C, 60.85; H, 6.16. Calcd. for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92%).

In a similar manner other cyclopropanes (1*R**,2*R**)-**6b-h** were prepared by acylations of (1*R**,2*R**)-**3b-d** using methyl alkanoate **4** or acyl chloride **5**, and the physical data obtained are summarized below.

(1R,2R*)-1-Butanoyl-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-6b.* Yields 75% (using methyl butanoate **4b**) and 66% (using butanoyl chloride **5b**); a viscous liquid, IR (neat/cm^{-1}) ν_{max} 1702, 1448, 1307 and 1146; ^{1}H NMR δ 0.82 (t, *J*=7.1 Hz, 3 H), 1.08 (d, *J*=6.4 Hz, 3 H), 1.22 (m, 2 H), 1.61 (dd, *J*=7.6, 5.2 Hz, 1 H), 1.78 (dd, *J*=9.6, 5.2 Hz, 1 H), 2.34 (m, 1 H), 2.67 (m, 1 H), 2.93 (m, 1 H) and 7.51-7.85 (m, 5 H)(Found: C, 63.37; H, 6.64. Calcd. for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81%).

By the similar acylation (using **4b**) of (1*S**,2*R**)-**3b** in place of (1*R**,2*R**)-**3b** (1*R**,2*R**)-**6b** was obtained as a sole product in 77% yield.

(1R,2R*)-1-(2-Methylpropanoyl)-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*, 2R*)-6c.* Yields 95% (using methyl 2-methylpropanoate **4c**) and 71% (using 2-methylpropanoyl chloride **5c**); a viscous liquid, IR (neat/cm^{-1}) ν_{max} 1698, 1448, 1307 and 1141; ^{1}H NMR δ0.86 (d, *J*=6.5 Hz, 3 H), 1.06 (d, *J*=6.7 Hz, 6 H), 1.77 (dd, *J*=8.0, 5.0 Hz, 1 H), 1.92 (dd, *J*=9.8, 5.0 Hz, 1 H), 2.39 (m, 1 H), 3.39 (sept, *J*=6.7 Hz, 1 H) and 7.52-7.86 (m, 5 H)(Found: C, 62.93; H, 6.73. Calcd. for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81%).

(1R,2R*)-1-Octanoyl-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-6d.* Yields 72% (using methyl octanoate **4d**) and 53% (using octanoyl chloride **5d**); a viscous liquid, IR (neat/cm^{-1}) ν_{max} 1704, 1316 and 1148; ^{1}H NMR δ 0.87 (t, *J*=6.6 Hz, 3 H), 1.08 (d, *J*=6.2 Hz, 3 H), 1.12-1.50 (br, 10 H), 1.61 (dd, *J*=7.6, 5.1 Hz, 1 H), 1.78 (dd, *J*=9.8, 5.1 Hz, 1 H), 2.37 (m, 1 H), 2.65 (m, 1 H), 2.93 (m, 1 H) and 7.51-7.84 (m, 5 H)(Found: C, 67.36; H, 8.19. Calcd. for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13%).

(1R,2R*)-1-Benzoyl-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-6e.* Yield 92%; a colorless solid, mp 110 °C; IR (Nujol/cm^{-1}) ν_{max} 1678, 1307 and 1141; ^{1}H NMR δ 1.02 (d, *J*=6.4 Hz, 3 H), 1.37 (dd, *J*=7.2, 5.6 Hz, 1 H), 2.00 (dd, *J*=9.6, 5.6 Hz, 1 H), 2.37 (m, 1 H) and 7.42-8.00 (m, 10 H)(Found: C, 68.05; H, 5.38. Calcd. for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37%).

(1R,2R*)-1-Butanoyl-2-propyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-6f.* Yield 63%; a viscous liquid; IR (neat/cm^{-1}) ν_{max} 1702, 1447, 1307 and 1146; ^{1}H NMR δ 0.87 (t, *J*=6.6 Hz, 3 H), 0.89 (t, *J*=6.6 Hz, 3 H), 1.12-1.50 (br, 6 H), 1.61 (dd, *J*=7.2, 5.2 Hz, 1 H), 1.78 (dd, *J*=9.6, 5.2 Hz, 1 H), 2.37 (m, 1 H), 2.68 (m, 1 H), 2.87 (m, 1 H) and 7.42-8.00 (m, 5 H)(Found: C, 65.47; H, 7.24. Calcd. for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53%).

(1R,2R*)-1-Butanoyl-2-phenyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-6g.* Yield 74%; a viscous liquid; IR (neat/cm^{-1}) ν_{max} 1702, 1447, 1307 and 1146; ^{1}H NMR δ 0.87 (t, *J*=6.5 Hz, 3 H), 1.22 (m, 2 H), 1.37 (dd, *J*=7.2, 5.5 Hz, 1 H), 2.00 (dd, *J*=9.6, 5.5 Hz, 1 H), 2.37 (m, 1 H), 2.67 (m, 1 H), 2.94 (m, 1 H) and 7.42-8.00 (m, 10 H)(Found: C, 69.40; H, 6.01. Calcd. for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14%).

(1R,2R*)-1-Benzoyl-2-phenyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-6h.* Yield 86%; a colorless solid; mp 144 °C; IR (Nujol/cm^{-1}) ν_{max} 1678, 1305 and 1143; ^{1}H NMR δ 1.56 (dd, *J*=8.8, 11.3 Hz, 1 H), 2.11 (dd, *J*=8.8, 13.4 Hz, 1 H), 3.29 (dd, *J*=11.3, 13.4 Hz, 1 H) and 6.82-8.00 (m, 15 H)(Found: C, 72.78; H, 4.94. Calcd. for $C_{22}H_{18}O_3S$: C, 72.90; H, 5.01%).

Preparation of (1R,2R*)-1-(1-hydroxyalkyl)-2-alkyl-1-(phenylsulfonyl)cyclopropanes (1R*,2R*)-8*

General Procedure: Upon treatment of (1*R**,2*R**)-**3b** with butyllithium and then butanal in a similar fashion to that described above two diastereoisomeric products were revealed to be formed by TLC and HPLC. Purification by column chromatography [silica gel, eluent hexane-ethyl acetate (3:1)] afforded a diastereoisomeric mixture of (1*R**,2*R**)-1-(1-hydroxybutyl)-2-methyl-1-(phenylsulfonyl)cyclopropane (1*R**,2*R**)-**8b** in 87% yield: a viscous liquid; diastereomer ratio=55/45 (HPLC); IR (neat/cm^{-1}) ν_{max} 3528, 1302 and 1140; ^{1}H NMR δ 0.75 (t, *J*=7.3 Hz, 3 H), 0.92 & 0.95 (dd, *J*=5.6, 7.1 Hz, 2 H), 1.10-1.74 (m, 4 H), 1.30 (d, *J*=6.6 Hz, 3 H), 1.67 & 1.77 (dd, *J*=5.6, 10.0 Hz, 1 H), 2.05 & 2.08 (m, 1 H), 3.43 & 3.66 (dd, *J*=4.3, 9.6 Hz, 1 H), 3.66 (br s, 1 H) and 7.52-7.91 (m, 5 H)(Found: C, 62.40; H, 7.76. Calcd. for $C_{14}H_{20}O_3S$: C, 62.65; H, 7.51%).

When (1*S**,2*R**)-**3b** was used in place of (1*R**,2*R**)-**3b**, (1*R**,2*R**)-**8b** was isolated in 85% yield (diastereomer ratio=56/44).

To a stirred mixture of PCC (1.08 g, 5 mmol) in dichloromethane (50 mL) was added a solution of (1*R**,2*R**)-**8b** (1 mmol) in dichloromethane (5 mL) at 0 °C, and stirring was continued for 6 h after which ethyl acetate (50 mL) and anhydrous $MgSO_4$ (10 g) was added. The mixture was further stirred for 10 min and then TLC showed the formation of a single product (1*R**,2*R**)-**6b**. After filteration and removal of the solvents, column chromatography [silica gel, eluent hexane-ethyl acetate (3:1)] gave (1*R**,2*R**)-**6b** in 81% yield.

In a similar manner other cyclopropanes (1*R**,2*R**)-**8c-8h** were obtained from (1*R**,2*R**)-**3b-d** using 2-methylpropanal, octanal, or benzaldehyde. Similar oxidations of (1*R**,2*R**)-**8c-8h** by the use of PCC afforded the corresponding (1*R**,2*R**)-**6c-6h** in high yields. The physical data of (1*R**,2*R**)-**8c-8h** are summarized below.

(1R,2R*)-1-(1-Hydroxy-2-methylpropyl)-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-8c*. Yield 71%; a viscous liquid; diastereomer ratio=57/43 (HPLC); IR (neat/cm^{-1}) ν_{max} 3530, 1288 and 1137; ^{1}H NMR δ 0.41 & 0.98 (d, *J*=6.6 Hz, 6 H), 0.81 & 0.90 (dd, *J*=5.6, 7.1 Hz, 1 H), 1.27 (d, *J*=6.4, 3 H), 1.72 & 1.86 (dd, *J*=5.8, 9.8 Hz, 1 H), 1.75 & 1.93 (m, 1 H), 2.08 & 2.21 (m, 1 H), 2.32 (br s, 1 H), 3.38 (m, 1 H) and 7.53-7.91 (m, 5 H)(Found: C, 62.77; H, 7.69. Calcd. for $C_{14}H_{20}O_3S$: C, 62.65; H, 7.51%).

(1R,2R*)-1-(1-Hydroxyoctyl)-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-8d*. Yield 86%; a viscous liquid; diastereomer ratio=69/31 (HPLC); IR (neat/cm^{-1}) ν_{max} 3532, 1308 and 1146; ^{1}H NMR δ 0.75 & 0.93 (dd, *J*=5.7, 7.1 Hz, 1 H), 0.85 & 0.86 (t, *J*=7.2 Hz, 3 H), 1.03-1.20 (m, 12 H), 1.25 & 1.31 (d, *J*=6.4 Hz, 3 H), 1.68 & 1.78 (dd, *J*=5.7, 10.0 Hz, 1 H), 2.11 & 2.35 (m, 1 H), 4.70 (br s, 1 H), 3.40 & 3.64 (dd, *J*=4.5, 9.7 Hz, 1 H) and 7.52-7.89 (m, 5 H)(Found: C, 66.96; H, 8.87. Calcd. for $C_{18}H_{28}O_3S$: C, 66.63; H, 8.70%).

(1R,2R*)-1-(α-Hydroxybenzyl)-2-methyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-8e*. Yield 96%; a viscous liquid; diastereomer ratio=57/43 (HPLC); IR (neat/cm^{-1}) ν_{max} 3535, 1300 and 1140; ^{1}H NMR δ 0.88 & 1.26 (dd, *J*=5.5, 7.2 Hz, 1 H), 1.36 & 1.39 (d, *J*=6.7 Hz, 3 H), 1.78 & 1.94 (dd, *J*=5.5, 10.0 Hz, 1 H), 2.19 & 2.48 (ddd, *J*=5.7, 6.7, 10.0 Hz, 1 H) and 3.93 & 4.10 (m, 1 H), 4.68-5.15 (br s, 1 H), and 6.97-8.09 (m, 10 H)(Found: C, 67.71; H, 5.88. Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00%).

(1R,2R*)-1-(1-Hydroxybutyl)-2-propyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-8f*. Yield 74%; a viscous liquid; diastereomer ratio=58/42 (HPLC); IR (neat/cm^{-1}) ν_{max} 3530, 1302 and 1140; ^{1}H NMR δ 0.76 & 0.90 (dd, *J*=5.8, 7.0 Hz, 1 H), 0.85 & 0.86 (t, *J*=7.1 Hz, 3 H), 0.89 (t, *J*=7.0 Hz, 3 H), 1.03-1.20 (m, 8 H), 1.68 & 1.78 (dd, *J*=6.0, 10.0 Hz, 1 H), 2.11 & 2.35 (m, 1 H), 3.40 & 3.64 (dd, *J*=4.6, 8.8 Hz, 1 H), 4.70 (br s, 1 H) and 7.52-7.89 (m, 5 H)(Found: C, 64.72; H, 8.55. Calcd. for $C_{16}H_{24}O_3S$: C, 64.83; H, 8.16%).

(1R,2R*)-1-(1-Hydroxybutyl)-2-phenyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-8g*. Yield 74%; a colorless solid; mp 74 °C; diastereomer ratio=55/45 (HPLC); IR (Nujol/ cm^{-1}) ν_{max} 3535, 1302 and 1140; ^1H NMR δ 0.62 & 0.99 (t,*J*=7.3, 3 H), 1.10-1.81 (m, 4 H), 1.47 & 1.76 (dd, *J*=6.2, 7.4 Hz, 1 H), 2.13 & 2.24 (dd, *J*=6.1, 9.8 Hz, 1 H), 2.74 (br s, 1 H), 2.87 & 2.92 (m, 1 H), 3.30 & 3.25 (dd, *J*=7.8, 9.8 Hz, 1 H) and 7.13-8.04 (m, 10 H)(Found: C, 69.46; H, 6.87. Calcd. for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71%).

(1R,2R*)-1-(α-Hydroxybenzyl)-2-phenyl-1-(phenylsulfonyl)cyclopropane (1R*,2R*)-8h*. Yield 86%; a colorless solid; diastereomer ratio=53/47 (HPLC); IR (Nujol/cm^{-1}) ν_{max} 3535, 1300 and 1140; ^1H NMR δ 1.85 & 1.99 (dd, *J*=6.1, 8.3 Hz, 1 H), 2.11 & 2.35 (dd, *J*=6.1, 10.1, 1 H), 3.40 & 3.68 (dd, *J*=8.3, 10.1 Hz, 1 H), 3.93 & 4.10 (dd, *J*=8.2, 9.0 Hz, 1 H), 6.52 (br s, 1 H) and 6.82-7.94 (m, 15 H)(Found: C, 72.68; H, 5.52. Calcd. for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53%).

Protonation of carbanion generated from (1S,2R*)-3b*

To a stirred solution of (1*S**,2*R**)-**3b** (0.39 g, 2.0 mmol) in dry THF (20 mL) was added dropwise butyllithium (1.67 mol/L in hexane, 1.50 mL, 2.4 mmol) at -78 °C under Ar, and stirring was continued for 10 min at -78 °C after which saturated aqueous NH_4Cl (5 mL) was added to the solution.The resultant solution was stirred for 10 min and then allowed to warm to room temperature for a period of 1 h. The aqueous layer was extracted with ethyl acetate (30 mL), and the combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. TLC of the residue revealed no recovery of (1*S**,2*R**)-**3b**. Column chromatography [silica gel, eluent hexane-ethyl acetated (4:1)] gave (1*R**,2*R**)-**3b** (0.38 g, 97 %).

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