Benzotriazole-Mediated Synthesis of 2,3-Disubstituted Allylic Alcohols

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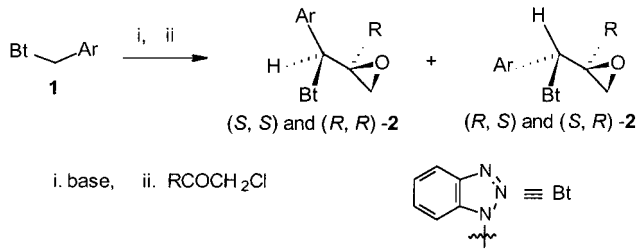
Introduction

During the past decade, benzotriazole was widely used as a synthetic auxiliary for introducing diverse organic functionality.[1] A survey of the literature inter alia shows that benzotriazole-mediated reactions with acyl or aroyl halides initially undergo two types of reaction: nucleophilic displacement of halides,[2−4] and nucleophilic attack on the carbonyl carbon, followed by displacement of halides concomitant with the formation of oxiranes.[5] Since treatment of 1-(arylmethyl)benzotriazoles **1** with strong bases such as LDA and *n*-BuLi in THF generates a carbanion at α-carbon bonded to N-1,[1] it is expected that reactions of the carbanion with α-monohalo ketones would give a mixture of diastereomers (*R*,*S*)- and (*S*,*R*)-, and (*R*,*R*)- and (*S*,*S*)-1-alkyl (or aryl)-1-[(aryl)(benzotriazol-1-yl)methyl]oxiranes **2** (Scheme 1). These may be utilized as precursors for allylic alcohols having specific substituents at C-2 and C-3 by introducing a radical or a carbanion at α-carbon bonded to N-1 upon removal of a benzotriazole moiety.

Synthesis of 2,3-disubstituted allylic alcohols has been mainly achieved by three methods: The first method involves regio- and stereospecific anti additions of Grignard reagents in the presence of cuprous iodide into propargyl alcohols, giving γ-functionally substituted vinylmagnesium compounds, which subsequently reacts with alkyl halides to give 2,3-dialkyl-substituted allylic alcohols with (*E*)-configuration.[6] Alternatively, iodination of the vinylmagnesium compounds followed by addition of Grignard reagents in the presence of $(PPh_3)_2NiCl_2$ gives allylic alcohols.[7] This is the only method to give 2,3-diaryl-, 2,3-dialkyl-, 2-alkyl-3-aryl-, and 2-aryl-3-alkyl-substituted allylic alcohols, and the reaction proceeds with high stereoselectivity. The second method involves isomerization of substituted oxiranes into allylic alcohols

Scheme 1



using diverse bases such as diethylaluminum 2,2,6,6-tetramethylpiperidide (DATMP),[8] a mixture of lithium diisopropylamide, and *t*-BuOK (LIDAKOR reagent),[9] and methylmagnesium *N*-cyclohexylisopropylamide.[10] The resulting double bonds prefer (*E*)-configuration. However, treatment of 1-methyl-1-vinyloxirane with alkyllithium in the presence of tertiary amine or lithium alkoxide gave allylic alcohols with (*Z*)-configuration predominant.[11] The third method involves alkylation of allylic sulfones, followed by the reductive elimination of the derived diastereomeric epoxysulfones, which results in predominant (*E*)-isomers.[12] The latter two methods are concerned with 2- and/or 3-aryl-substituted allylic alcohols. Besides, regioselective reduction of α,β-unsaturated carbonyl compounds by vapor phase hydrogen-transfer over an $MgO-B_2O_3$ (Mg/B = 100/2) catalyst using secondary alcohols as a hydrogen donor,[13] and oxidation of allylselenides with 15%-H_2O_2 in the presence of pyridine in CH_2Cl_2 at 0 °C[14] are reported to give 2- and/or 3-substituted allylic alcohols. However, the former yields saturated alcohols and saturated aldehydes as byproducts depending on the substituents at α and β positions of the carbonyl compounds, whereas the latter appears to be preferable to the preparation of allylic alcohols without a substituent at the terminal olefinic carbon atom. In addition, oxidation of allylic phenyl tellurides may be utilized for the preparation of 1-phenylallylic alcohols.[15] However, it is uncertain whether the method serves our purpose or not. Therefore, it may be worthwhile to exploit a new method for the synthesis of allylic alcohols with specific substituents at C-2 and C-3. With this in mind, the reactions of **1** with a base have been studied. The results are described herein.

Results and Discussion

Compounds **1** were prepared by a documented procedure,[16] and treatment of **1** with LDA in THF at −78 °C for 5 min, followed by addition of 1-chloro-3,3-dimethyl-2-butanone, gave a mixture of diastereomers **2** (R = *t*-Bu)

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Table 1. Quantities of Reactants and Yields and Melting Points of 2

	$BtCH_2Ar$		$RCOCH_2Cl$		time	(*R*,*S*)-**2**		(*R*,*R*)-**2**	
compd	Ar	mmol	R	mmol	(min)	yield[a] (%)	mp (°C)	yield[a] (%)	mp (°C)
a	Ph	2.69	*t*-Bu	3.23	5	5	198−200[b]	25	133−134[c]
		1.43		1.50	15	8		23	
b	3-$MeOC_6H_4$	2.58	*t*-Bu	2.58	5	3	204−206[b]	20	122−123[e]
c	3-MeC_6H_4	0.730	*t*-Bu	0.730	5	4	182−184[c]	18	liquid
		1.34		1.41	15	5		27	
d	3,4-$Me_2C_6H_3$	1.27		1.27	5			23	liquid
		1.48		1.55	15			20	
e	3-$PhOC_6H_4$	1.18	*t*-Bu	1.18	5	11	170−171[b]	45	104−106[c]
f	2-Pyridyl	1.62	*t*-Bu	1.62	5	30	197−198[b]	57	105−106[c]
g	3-Pyridyl	0.866	*t*-Bu	0.866	5	22	204−206[b]	24	171−172[c]
h	6-Me-2-pyridyl	2.20	*t*-Bu	2.20	5	42	181−182[b]	55	121−122[d]
i	Ph	2.75	Ph	2.75	5	10	166−167[b]	31	172−173[b]
j	Ph	2.61	3-MeC_6H_4	2.61	5	19	liquid	29	192−194[b]
k	Ph	2.60	2,5-$Me_2C_6H_3$	2.60	10	8	114−115[d]	27	97−98[c]
		1.43		1.51	15	10		35	
l	3-MeC_6H_4	2.64	2,5-$Me_2C_6H_3$	2.64	10	9	163−164[b]	14	126−128[c]
		4.48		4.93	15	37		26	
m	3-$MeOC_6H_4$	1.88	2,5-$Me_2C_6H_3$	1.88	10	6	110−111[c]	45	99−111[c]

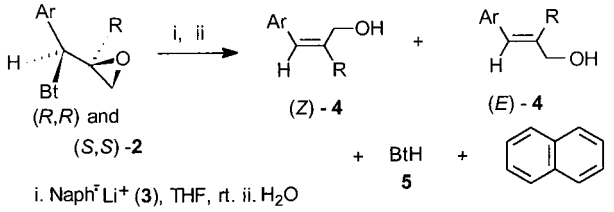
[a] Isolated yields. [b] MeOH was used for recrystallization. [c] *n*-Hexane was used for recrystallization. [d] A mixture of *n*-hexane and CH_2Cl_2 was used for recrystallization. [e] A mixture of *n*-hexane and EtOAc was used for recrystallization.

(R_f = 0.5 and 0.4, *n*-hexane and EtOAc = 5:1). The diastereomers **2** were separated by chromatography on a silica gel column. The former with a higher R_f value was assigned to be an enantiomeric mixture [abbreviated as (*R*,*R*)] with *R* and *R* configurations. The latter with a lower R_f value was an enantiomeric mixture [abbreviated as (*R*,*S*)] with *R* and *S* configurations. Selected compounds **1** (**1a**,**c**−**d**,**k**−**l**) were treated with LDA for 15 min, and then the mixtures were subjected under the same conditions as mentioned above. However, the yields of **2** were not much different. The quantities of reactants, the yields, and melting points of diastereomers (*R*,*S*)-**2a**−**h** and (*R*,*R*)-**2a**−**h** are summarized in Table 1.

The structures of the diastereomers of **2a**−**h** were determined on the basis of the spectroscopic (^{1}H NMR, IR, and MS) data and elemental analyses. The ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **2a** exhibited absorption at 146.1, 136.4, 134.3, 129.7, 129.3, 129.1, 127.8, 124.2, 120.4, 111.1, 64.0, 63.3, 49.0, 34.7, 27.5 ppm, which can be identified with the structure **2a**. The stereochemistry of diastereomers **2a**−**h** was assigned based on the X-ray crystallographic analysis of the major product **2a** (Supporting Information). The figure in the Supporting Information clearly shows that the bulky benzotriazole moiety and *tert*-butyl group are anti. Consequently the major compound **2a** is an enantiomeric mixture of (*R*,*R*)- and (*S*,*S*)-configurations. Judging from this, the minor compound should be an enantiomeric mixture having (*R*,*S*)- and (*S*,*R*)- configurations. By analogy with **2a**, compounds **2b**−**h**, which are major products, would be enantiomeric mixtures with (*R*,*R*)- and (*S*,*S*)- configurations and the minor compounds **2b**−**h** would be enantiomeric mixtures with (*R*,*S*)- and (*S*,*R*)-configurations.

To remove a benzotriazole moiety,[17] concomitant with generation of a radical center at the α-carbon bonded to N-1, lithium naphthalenide **3**, which is a well-known one-electron donor[18] was added to a solution of (*R*,*R*)-**2a**−**h** in THF until the dark color of **3** prevailed. The reaction

Scheme 2



proceeded smoothly to give (*Z*)-3-aryl-2-(*tert*-butyl)-2-propenol **4a**−**h** together with a minute amount of the (*E*)-isomers (*E*)-**4a**−**d**, benzotriazole **5**, naphthalene, and an unknown mixture (Scheme 2). However, no (*E*)-isomers were obtained from the reactions with **2f**−**h**. Similarly, treatment of (*R*,*S*)-**2a** (0.0651 mmol) with **3** (0.112 mmol) under the same conditions gave (*Z*)- **4a** (65%), (*E*)-**4a** (5%), and **5** (77%). Unexpectedly, it was found that the reaction of (*R*,*R*)-**2e** under the same conditions gave (*Z*)- and (*E*)-**4a** instead of the corresponding (*Z*)-and (*E*)-2-(*tert*-butyl)-3-(3-phenoxyphenyl)-2-propenols **4** (Ar = 3-$PhOC_6H_4$). Since we were unaware of the dephenoxylation of aryl phenyl ether by **3**, diphenyl ether (1.257 mmol) was treated with **3** (2.011 mmol) in THF (5 mL) under the same foregoing condition. From the reaction mixture were isolated phenol (45%), unreacted ether (13%), and unknown mixtures. This result indicates that (*Z*)-**4a** can be formed from (*R*,*R*)-**2e**. However, the mechanism for the dephenoxylation of **2e** is uncertain. Quantities of reactants, (*R*,*R*)-**2a**−**h** and **3**, and yields of (*Z*)-**4a**−**h** and (*E*)-**4a**−**d** are summarized in Table 2.

The stereochemistry of **4** was determined based on a NOESY spectrum of (*Z*)-**4b** (Ar = 3-$MeOC_6H_4$) (Figure 1), which shows interactions between the vinyl proton and the protons of the *tert*-butyl group, and between the methoxy protons and the methylene protons. Furthermore, the NOESY spectrum shows an interaction between the methylene protons and the protons at C-2 and C-6 of the 3-anisyl group, indicating a trans relationship between the two bulky groups, i.e., *tert*-butyl and 3-anisyl groups.

The stereoselective formation of (*Z*)-**4a**−**h** may be understood by examination of the transition state in a Newman projection (Scheme 3). One electron-transfer from **3** to **2** would form an anion radical of **2**. The most

(17) Benzotriazole has been reported to accept at least four electrons: Refer to Wamhoff, H. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W. Eds.; Pergamon Press: Oxford, 1984; Vol. 5, 4. 11, p 689.

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Table 2. Quantities of Reactants 2 and 3, and Yields of 4 and 5

		(*R*,*R*) and (*S*,*S*)-**2**			**3**				
entry	compd	Ar	R	mmol	mmol	compd	(Z)-**4**	(E)-**4**	**5**
1	**a**	Ph	*t*-Bu	0.345	0.569	**a**	59	6	
2	**b**	3-$MeOC_6H_4$	*t*-Bu	0.267	0.427	**b**	54	7	
3	**c**	3-MeC_6H_4	*t*-Bu	0.261	0.417	**c**	43	6	
4	**d**	3,4-$Me_2C_6H_3$	*t*-Bu	0.280	0.462	**d**	54	7	
5	**e**	3-$PhOC_6H_4$	*t*-Bu	0.315	0.519	**e**	40	5	
6	**f**	2-Pyridyl	*t*-Bu	0.318	0.525	**f**	53		
7	**g**	3-Pyridyl	*t*-Bu	0.295	0.487	**g**	67		
8	**h**	6-Me-2-pyridyl	*t*-Bu	0.344	0.567	**h**	47		
9	**i**	Ph	Ph	0.391	0.635	**i**	28	32	77
10	**j**	Ph	3-MeC_6H_4	0.492	0.597	**j**	21	13	51
11	**k**	Ph	2,5-$Me_2C_6H_3$	0.287	0.597	**k**	54	20	74
12	**l**	3-MeC_6H_4	2,5-$Me_2C_6H_3$	0.492	0.597	**l**	47	32	81
13	**m**	3-$MeOC_6H_4$	2,5-$Me_2C_6H_3$	0.322	0.597	**m**	47	14	83
14	**n**	Ph	Me	0.452	0.678	**n**	39	40	61

[a] Isolated yields. (*E*)- and (*Z*)-**4** are all liquids.

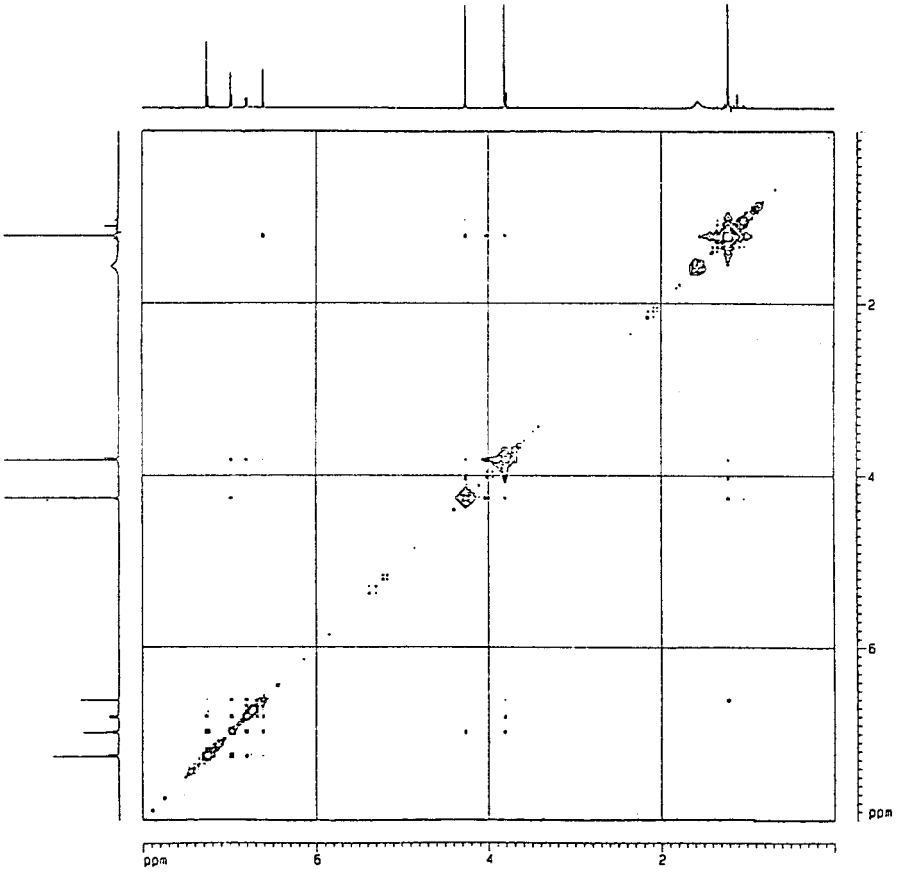


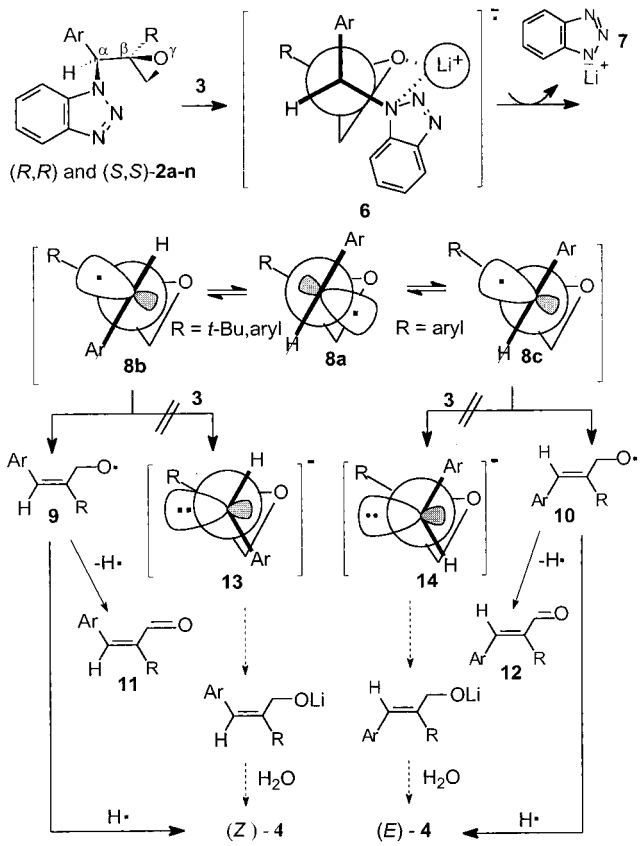
Figure 1. NOESY spectrum of (*Z*)-3-(3-anisyl)-2-(*tert*-butyl)-2-propenol (*Z*)-**4b**.

favorable conformation around α-C of an anion radical of **2** is shown in the intermediate **6** in which the two bulky groups, i.e., the *tert*-butyl and benzotrizole moieties, are anti. The interaction of Li^+ ions with nonbonding electrons on the oxygen and N-1 atoms would be expected to facilitate the formation of such a gauche type arrangement.[19] The rapid extrusion of the stable benzotriazolate ion **7** from the anion radical **6** initially generates the benzylic radical **8a** whose unpaired electrons should push the other two bonding orbitals (C−Ar and C−H) away so that the steric hindrance between Ar and R groups in **8a** will be much more important than that in the conformational isomer **8b**. Severe steric repulsion due to the close proximity between *tert*-butyl and aryl groups in the transition state would cause the C−C bond rotation to select the conformer **8b** as a preferable conformer. Since the opening of epoxides to a radical center is a common reaction,[20] the formation of *β*,*γ*-unsaturated alkoxy radicals **9** and **10** from **8b** and **8c**, respectively, is conceivable. Intermolecular hydrogen abstraction of **9** would give (*Z*)-**4**. Since small amounts of (*E*)-**4** were isolated, the transition state leading to **10** would be highly energetic, presumably due to severe

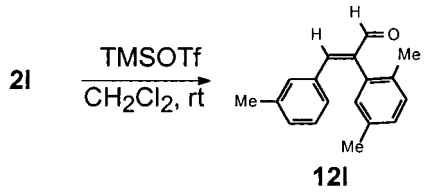
(19) We have proposed the involvement of Li^+ in the formation of 2-(2-arylethyl)-5-methyltetrahydrofurans from 2-[2-aryl-2-(benzotriazol-1-yl)ethyl]-5-(methyl)tetrahydrofurans and **7**: Refer to Kang, Y. H.; Kim, K. *Tetrahedron* **1999**, *55*, 4271.

(20) Fossey, J.; Lefort, D.; Sorba, J. *Free radicals in Organic Chemistry*; John Wiley and Sons: New York, 1995; Chapter 13, pp 151−165.

Scheme 3



Scheme 4



steric repulsion between *tert*-butyl and Ar groups which are cis each other. On the other hand, when R is an aryl group, which is less bulky than *tert*-butyl, conformers **8b** and **8c** would be in equilibrium, from which geometric isomers (*E*)- and (*Z*)-**4** would result (vide infra). In fact, when R = Me, the corresponding (*E*)- and (*Z*)-**4n** (Ar = Ph, R = Me) were isolated in 40% and 39% yields, respectively.

To confirm the involvement of the cleavage of the C−O bond of epoxides **8b** and **8c** in a radical mechanism, **2l** (0.244 mmol) was treated with **3** (1 equiv) for 5 min under the same conditions as described. From the reaction mixture were isolated (*Z*)- (46%) and (*E*)-**4l** (32%), **5** (66%), and unknown mixtures (27 mg) showing many spots on TLC (R_f = 0.8, 0.7, 0.6, 0.5, EtOAc: *n*-hexane = 1:10). No unreacted **2l** was recovered. The GC−MS spectrum (retention time = 11.4 min, HP−Ultra 1 column, 0.2 mm × 30 m, EI) of one (R_f = 0.5) of the unknown fractions exhibited a mass number, m/z = 250, corresponding to the molecular weight of (*E*)-2-(2,5-dimethylphenyl)-3-(3-tolyl)acrolein **12l**. The IR (neat) spectrum of the fraction exhibited a carbonyl absorption at 1673 cm^{-1}. The ^1H NMR (300 MHz, $CDCl_3$) spectrum showed a singlet at 9.76 ppm, indicating the existence of a formyl group. All of these data were consistent with those of the authentic sample **12l** (Ar = 3-MeC_6H_4, R = 2,5-$Me_2C_6H_3$), which was prepared by treatment of **2l** with TMSOTf in CH_2Cl_2 at room temperature. The stereochemistry of **12l** was assigned based on that of the known **12i** (Ar = R = Ph),[21] whose mp (94 °C) and spectroscopic (^1H NMR, IR, MS) data were in good agreement with those of **12i** (mp, 92−93 °C) prepared according to the procedure for **12l**.

The spectroscopic data coupled with the failure to isolate unreacted **2l** support the formation of compounds (*E*)- and (*Z*)-**4** via a radical mechanism. Stabilization of conjugated aldehydes **11** and **12** may be the driving force for oxidation of **8b** and/or **8c**. Based on this result, a possible SET reaction of **8** to generate carbanions **13** and **14**, followed by heterolytic cleavage of C−O bond to give eventually (*E*)- and (*Z*)-**4**, is unlikely.

Similarly a mixture of diastereomers (R = aryl) (R_f = 0.5 and 0.4, *n*-hexane and EtOAc = 8:1) was separated by chromatography on a silical gel using a mixture of *n*-hexane and EtOAc (20:1). The former with a higher R_f value and the latter with a lower R_f value were assigned to be enantiomeric mixtures with (*R*,*R*)- and (*R*,*S*)-configurations, respectively. Interestingly, treatment of **2i**−**m** (Ar = R = aryl) with **3** under the same conditions as for **2a**−**h** gave a mixture of diastereomers *(Z)*-**4i**−**m** and *(E)*-**4i**−**m**, which were separated by chromatography. Yields of the diastereomers are summarized in Table 2. The structures of (*Z*)-**4i**−**m** and (*E*)-**4i**−**m** were determined by the same method as for *(Z)*-**4a**−**h**. The NOESY spectrum of (*Z*)-**4m** clearly shows the interactions between the methylene protons and the protons of the methoxy group. Entries 9−13 show that (*E*)- and (*Z*)-isomers are produced in the ratios of 3:1 to 1:1 when oxiranes **2i**−**m** have less bulkier aryl groups compared with the *tert*-butyl group at C-1 of the oxirane ring. In addition, Table 2 shows that the ratio of (*E*)- to (*Z*)-isomers decreases with further steric interactions between Ar and R groups (in the order of entries 9 > 10 > 11 > 12 > 13 > 1−8), which manifests the decrease of the population of the conformer **8c**, the inversion isomer of **8a**, in equilibrium with the conformer **8b**.

In conclusion, a method for the synthesis of 2-substituted 3-aryl-2-propen-1-ols has been developed by treatment of 1-alkyl (or aryl)-1-[(aryl)(benzotriazol-1-yl)methyl]-oxiranes with lithium naphthalenide in THF at room temperature. The stereochemistry around the C=C double bond depends on the bulkiness of the alkyl (or aryl) groups at C-1 of oxiranes, which originate from 1-alkyl (or aryl)-2-chloroethanones. The merit of the method lies in the chemoselective introduction of an alkyl or aryl group at C-2 and an aryl group at C-3 of allylic alcohols, which has been seldom explored hitherto.

Experimental Section

General Methods. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz in $CDCl_3$ solution containing Me_4Si as an internal standard, respectively. IR spectra were obtained in KBr or as thin films on KBr plates. GC-MS spectra were obtained by electron impact at 70 eV. Elemental analyses were carried out by the Korea Basic Science Institute. Column chromatography was performed using silica gel (70−230 mesh). Chromatograms were visualized by a mineral UV lamp. Melting points are uncorrected.

(21) (a) Gupton, J. T.; Polaski, C. M. *Synth. Commun.* **1981**, *11*, 561. (b) Payne, G. B.; Williams, P. H. *J. Org. Chem.* **1961**, *26*, 651.

General Procedure for the Synthesis of 1-Alkyl (or Aryl)-1-[(aryl)(benzotriazol-1-yl)methyl]oxiranes (2). To a solution of **1** (0.7−2.8 mmol) in THF (15 mL) at −78 °C was added LDA (1.1−4.0 mmol). The mixture was stirred for 5 min, followed by addition of 1-chloro-3,3-dimethyl-2-butanone (0.7−3.2 mmol). The mixture was additionally stirred for 10 min, followed by addition of water (50 mL), which was extracted with CH_2Cl_2 (50 mL × 3). The extracts were dried over $MgSO_4$. Removal of the solvent in vacuo gave a residue, which was chromatographed (3 × 13 cm), with a mixture of *n*-hexane and EtOAc (10:1) as eluent to give an enantiomeric mixture of (*R*,*R*) and (*S*,*S*)-1-[(aryl)(benzotriazol-1-yl)methyl]-1-(*tert*-butyl)oxiranes (**2**) [(*R*,*R*)-2] and an enantiomeric mixture of (*R*,*S*) and (*S*,*R*)-1-[(aryl)(benzotriazol-1-yl)methyl]-1-(*tert*-butyl)oxiranes (**2**) [(*R*,*S*)-2]. However, when 1-aryl-2-chloroethanones (1.2−2.8 mmol) were employed, the reaction mixture was eluted with the same solvent mixture (20:1) to give enantiomeric mixtures of (*R*,*R*)- and (*S*,*S*)-, and (*R*,*S*)- and (*S*,*R*)-1-aryl-1-[(aryl)(benzotriazol-1-yl)methyl]oxiranes (**2**). Quantities of reactants, and yields and melting points of (*R*,*R*)-**2**, and (*R*,*S*)-**2** are summarized in Table 1.

General Procedure for the Reactions of (*R*,*R*)-2 with Lithium Naphthalenide (3). To a solution of **2** (0.09−0.49 mmol) in THF (8 mL) was dropwise added **3** (0.19−0.64 mmol), prepared in situ by addition of lithium lump (76 mg, 10.9 mmol) to the stirred solution of naphthalene (866 mg, 6.76 mmol) in THF (30 mL) for 40 min at room temperature, using a hypodermic syringe. The mixture was stirred for an additional 5 min, followed by addition of water (50 mL), which was extracted with CH_2Cl_2 (50 mL × 3). The extracts were dried over $MgSO_4$ and worked up as usual. Chromatography (2 × 13 cm) of the reaction mixture using *n*-hexane gave naphthalene. Elution with a mixture of *n*-hexane and EtOAc (9:1) gave (*Z*)-3-aryl-2-(*tert*-butyl)-2-propenol (*Z*)-**4a**−**h.** Subsequent elution with the same solvent mixture gave (*E*)-**4a**−**d**. However, when **2i**−**m** were treated with **3**, (*E*)-**4i**−**m,** followed by (*Z*)-**4i**−**m** were eluted with a mixture of *n*-hexane and EtOAc (10:1). The aqueous layer was treated with concentrated HCl to give benzotriazole **5,** which was extracted with CH_2Cl_2. Consult Table 2 for quantities of the reactants, and yields of **4** and **5**.

Preparation of (*E*)-2-(2,5-Dimethylphenyl)-3-(3-tolyl)-acrolein (12l). To a solution of **2l** (80 mg, 0.217 mmol) in CH_2Cl_2 (5 mL) was added trimethylsilyl trifluoromethanesulfonate (48 mg, 0.217 mmol). The mixture was stirred for 5 h at room temperature, by the time no spot corresponding to **2l** (R_f = 0.5, EtOAc: *n*-hexane = 1:10) was observed on TLC. The mixture was quenched by the addition of water (5 mL), followed by extraction with CH_2Cl_2 (40 mL × 3). The combined extracts were dried over $MgSO_4$ and chromatographed on a silica gel column (3 × 10 cm). Elution with a mixture of EtOAc and *n*-hexane (1:7) gave **12l** (17 mg, 36%): yellow liquid; ^{1}H NMR δ 2.01 (s, 3H), 2.27 (s, 3H), 2.30 (s, 3H), 6.83 (s, 1H), 6.89 (d, J = 1.4 Hz, 1H), 7.00 (s, 1H), 7.08−7.22 (m, 5H), 7.40 (s, 1H), 9.80 (s, 1H); ^{13}C NMR δ 19.0, 21.0, 21.3, 127.4, 128.6, 129.3, 129.4, 130.4, 131.3, 131.7, 132.9, 133.3, 134.2, 135.9, 138.3, 141.8, 150.9, 194.2; IR (neat) 3024, 2928, 2704, 1677, 1610, 1446, 1168 cm^{-1}; MS *m*/*z* 250 (M^+, 100), 235 (31.4), 192 (30.0), 130 (57.4). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.42; H, 7.21.

X-ray Structure Analysis of Compound 2a. A single crystal of **2a** was obtained from CH_2Cl_2. The data were collected on an Enraf-Nomius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation. The structure was inferred by direct methods and subsequent Fourier maps. Refinements were carried out by full-matrix least-squares techniques. Non-hydrogen atoms were anisotropically refined. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*, Vol IV, 1974. All calculations and drawings were performed using a Micro VAX II Computer with an SDP system. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Supporting Information Available: Copies of ^{1}H NMR, IR, elemental analyses of **(***R*,*R*)-**2a**−**m**, (*R*,*S*)-**2a**−**m**, and (*Z*)-**4a**−**n**, (*E*)-**4i**−**n**; *X*-ray crystallographic data of **2a**; and an ORTEP drawing of an enantiomeric mixture of (*R*,*R*)-1-[(benzotriazol-1-yl)(phenyl)methyl]-1-(*tert*-butyl)oxiranes (**2a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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