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Generation of Enolates from α,β-Epoxy Sulfoxides with Lithium Dimethylcuprate: A Novel Synthesis of Aldols and Some Trial to Trap the Enolates(1)

Tsuyoshi Satoh, Atsushi Sugimoto, Masayuki Itoh, and Koji Yamakawa*
Faculty of Pharmaceutical Sciences, Science University of Tokyo,
Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162

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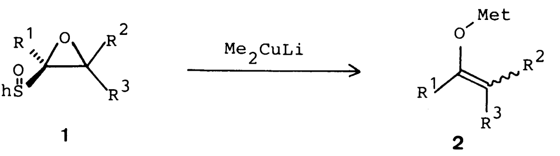
Enolates were generated from α,β-epoxy sulfoxides using lithium dimethylcuprate as an electron-transfer reagent. The enolates were trapped with several electrophiles, in which aldehydes reacted with the generated enolates giving aldols in good yields with high regioselectivity.

Enolates are the most fundamental intermediates in the chemistry of carbon–carbon bond formation. Such famous reactions as acetoacetic ester synthesis, aldol condensation, Claisen reaction, Dieckman condensation, Perkin reaction, and Robinson annulation are known to take place through enolates.(2) Usually, enolates are generated from carbonyl compounds with strong bases, such as sodium hydride, metal alkoxides, or lithium diisopropylamide (LDA). In modern organic syntheses some other methods for the generation of metal enolates have been reported.(3)

We recently reported novel synthetic methods from 1-chloroalkyl aryl sulfoxides and carbonyl compounds through α,β-epoxy sulfoxides **1**.(4) In a study it was found that the β-position of **1** shows quite a high reactivity to various kinds of nucleophiles. In a search for another nucleophiles we found that lithium dialkylcuprates reacts with α,β-epoxy sulfoxides **1** to give enolates **2** (Scheme 1).



Met= Cu or Li

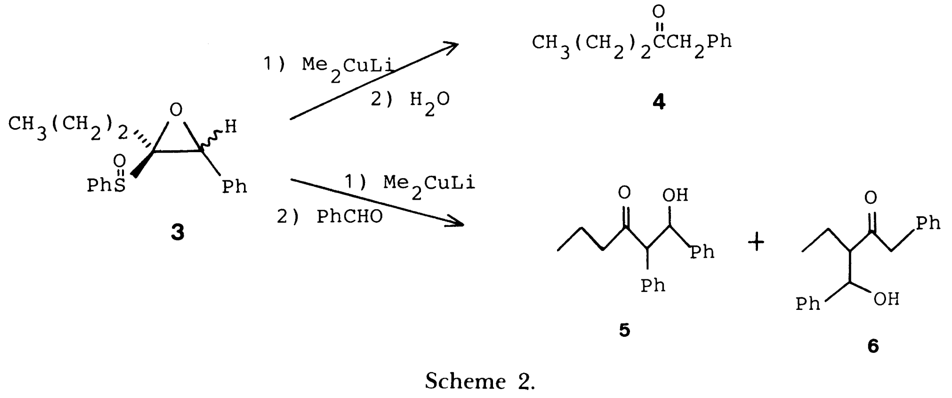
Scheme 1.

In this paper we report on details concerning a novel method for the generation of enolates **2** from **1** with lithium dimethylcuprate (Me_2CuLi) and the synthesis of aldols from **1**.(5) We also refer to some trials to trap the generated enolates with *t*-butyldimethylsilyl chloride, acetyl chloride, and ethyl chloroformate.

Results and Discussion

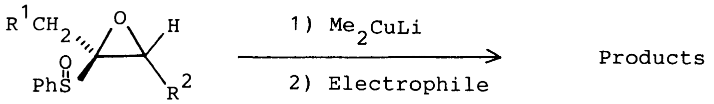
The nucleophilic ring-opening of oxiranes by organocopper reagents is a very useful method for carbon–carbon bond formation.(6) In some cases, however, the reaction of oxiranes with organocopper reagents shows a somewhat different aspect due to the electron-transferable nature of the reagents.(7) For instance, Tamao et al. recently reported the deoxygenation of α,β-epoxy silanes with Grignard reagents catalyzed by copper giving vinylsilanes.(8) This reaction was thought to proceed through a one-electron transfer from an organocopper reagent.

The treatment of α,β-epoxy sulfoxide **3**,(9) which was synthesized from 1-chlorobutyl phenyl sulfoxide and benzaldehyde, was carried out with two equivalents of Me_2CuLi in ether at 0 °C for 3 h. The reaction was quenched with aqueous NH_4Cl to give 1-phenyl-2-pentanone **4** in 77% yield as the sole product. Interestingly, no methylated product was obtained. Among the alkylcopper reagents studied (Me_2CuLi, Bu_2CuLi, $Bu_2CuCNLi$, $Et_2CuMgBr$) Me_2CuLi was found to be the most useful. As a copper source,

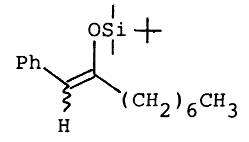
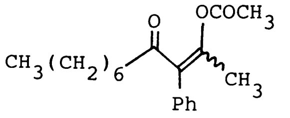
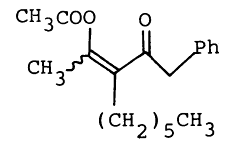
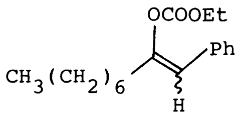
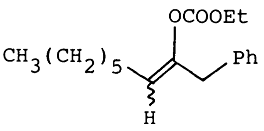


Scheme 2.

Table 1. Trapping the Generated Enolates from α,β-Epoxy Sulfoxides (**7** and **8**) with Electrophiles



7 R^1=$(CH_2)_5CH_3$; R^2=Rh
8 R^1=Ph; R^2=$(CH_2)_5CH_3$

Entry	α,β-Epoxy sulfoxide	Electrophile (equiv.)	Conditions[a]	Product	Yield[b] %
1	**7**	TBDMS-Cl (5)	Et_3N, HMPA 0°C—r.t. 9 h	 **9**	90
2	**8**	TBDMS-Cl (5)	Et_3N, HMPA 0°C—r.t. 17 h	**9**	85
3	**7**	CH_3COCl (10)	0°C (1.5 h) then r.t. 1 h	 **10**	53
4	**8**	CH_3COCl (10)	0°C, 1.5 h	 **11**	30
5	**7**	ClCOOEt (5)	0°C, 1.5 h	 **12**	50
6	**8**	ClCOOEt (5)	0°C, 1 h	 **13**	81

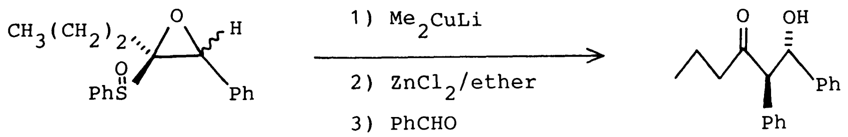
a) All reactions were carried out with three equivalents of Me_2CuLi in dry ether at 0°C then quenched with electrophile. b) Isolated yield after silica-gel column chromatography.

copper(I) bromide-dimethyl sulfide complex (CuBr·SMe_2)[10] was found to be the most effective. We thought that this reaction took place through an enolate. Indeed, by quenching the reaction with benzaldehyde instead of water, a mixture of aldols (**5** and **6**; **5**:**6**=1:4) was obtained in 41% yield (Scheme 2).[11]

In order to obtain further proof of the enolates, the reaction was carried out with other electrophiles using **7** and **8** as the α,β-epoxy sulfoxides. The reason for using **7** and **8** was to clarify the reactivity and regioselectivity of the generated enolates (Table 1).

Quenchig the enolates generated from **7** and **8** with chlorotrimethylsilane gave a mixture of silyl enol ethers; however their isolation was found to be difficult. With *t*-butyldimethylsilyl chloride, both enolates derived from **7** and **8** selectively gave a stereoisomeric mixture of silyl enol ether **9** in good yield, though the reaction was found to have no regiospecificity (Entries 1 and 2). The reaction of the enolates with acetyl chloride was somewhat interesting: it gave diacylated products (**10** and **11**) with high regioselectivity, though yields were not satisfactory (Entries 3 and 4). The reaction of the enolates with ethyl chloroformate regioselectively gave the enol carbonates (**12** and **13**) in moderate to good yields (Entries 5 and 6).

With some results of trapping the enolates with electrophiles in hand, our attention was again focused



3

Scheme 3.

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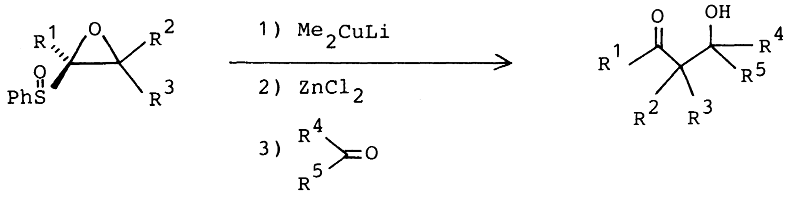
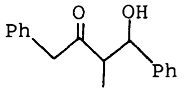
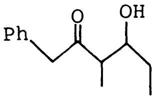
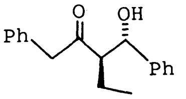
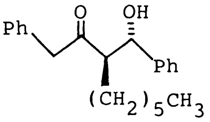
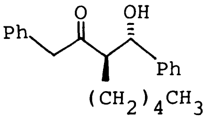
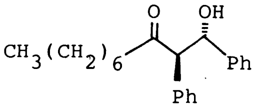
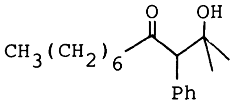
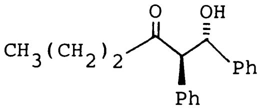
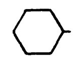
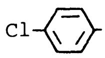
Table 2. Synthesis of Aldols from α,β-Epoxy Sulfoxides with Me_2CuLi and Carbonyl Compounds in the Presence of $ZnCl_2$



Entry	α,β-Epoxy sulfoxide			Carbonyl compound		Time[a]	Aldol		Yield[b]
	R^1	R^2	R^3	R^4	R^5				%
1	$PhCH_2$	CH_3	H	Ph	H	1.5 h[c]		**14**[e]	80
2	$PhCH_2$	CH_3	H	CH_3CH_2	H	1.5 h[c]		**15**[e]	79
3	$PhCH_2$	CH_3CH_2	H	Ph	H	2 h		**16**	53
4	$PhCH_2$	$CH_3(CH_2)_5$	H	Ph	H	7 h		**17**	60
5	$PhCH_2$	$CH_3(CH_2)_4$	H	Ph	H	4 h		**18**	74
6	$CH_3(CH_2)_6$	Ph	H	Ph	H	30 min		**19**	70
7	$CH_3(CH_2)_6$	Ph	H	CH_3	CH_3	30 min		**20**	52[f]
8	$CH_3(CH_2)_2$	Ph	H	Ph	H	40 min		**5**	74
9	$PhCH_2$	CH_3	CH_3	Ph	H	2 d[d]	—[g]		—
10			H	—	—	2 h[c]	—[h]		—

a) All reactions were carried out in ether at 0 °C. Unless otherwise noted, 3 equivalents of Me_2CuLi were used. b) Isolated yield. c) 4 equivalents of Me_2CuLi were used. d) 5 equivalents of Me_2CuLi were used. e) Threo/erythro=2/1. f) This reaction gave **20** with 1-phenyl-2-nonanone (39%). g) This reaction did not give aldol but 3-methyl-1-phenyl-2-butanone[4a] in 68% yield. h) The α,β-epoxy sulfoxide did not react with Me_2CuLi.

on the result with the carbonyl compound described above. As shown in Scheme 2, quenching the enolate obtained from **3** with benzaldehyde gave aldols **5** and **6** without regioselectivity. We thought that it is possible to obtain aldols with high regioselectivity if the reaction is carried out with some additives. House demonstrated that zinc chloride is quite useful as an additive for controling the aldol condensation.[12]

α,β-Epoxy sulfoxide **3** was treated with three equivalents of Me_2CuLi in ether at 0 °C for 40 min. After all of the starting materials disappeared, two equivalents of $ZnCl_2$ in ether[12a] followed by benzaldehyde were added to the reaction mixture. The desired aldol reaction took place quite smoothly to give **5** in 74% yield (Scheme 3). The stereochemical assignment of **5** was made by an examination of the vicinal coupling constant in the ^{1}H NMR. The coupling constant (J=9 Hz) of the proton at the carbon bearing a hydroxyl group clearly indicated that **5** was threo diastereomer.[12b,13] Though a trace amount of the erythro isomer was observed on ^{1}H NMR, this reaction was found to take place with complete regioselectivity. The representative examples of the synthesis of aldols from α,β-epoxy sulfoxides with Me_2CuLi and carbonyl compounds are listed in Table 2.

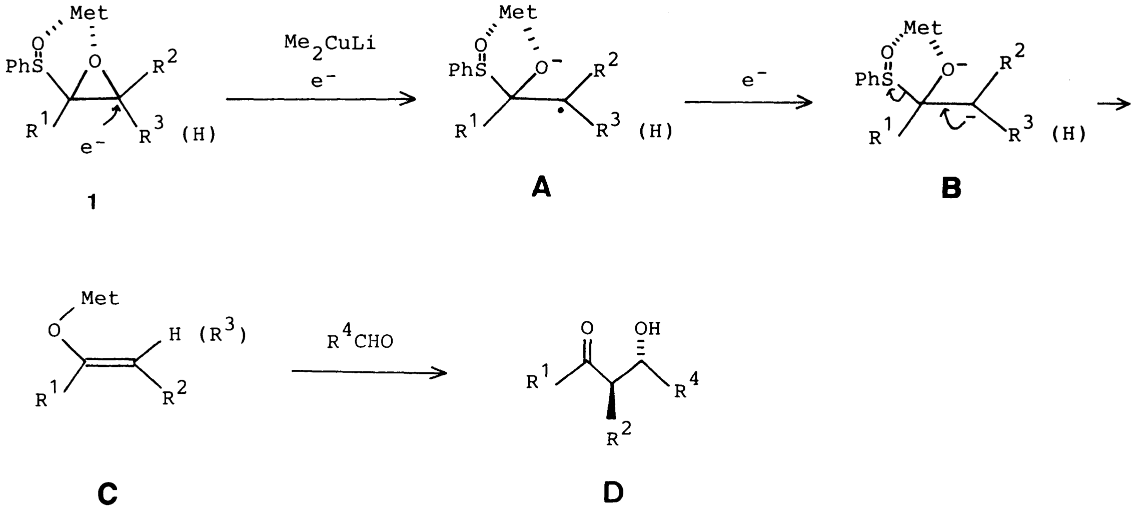
The important characteristics of the results shown in Table 2 are as follows: 1) The α,β-epoxy sulfoxides having a hydrogen at the β-carbon (R^3=H; they were synthesized from aldehydes) reacted smoothly with Me_2CuLi to give enolates in high yields, except Entry 10. 2) The α,β-epoxy sulfoxides having a branch at C-1 of R^1 showed quite a low reactivity with Me_2CuLi (Entry 10). 3) The α,β-epoxy sulfoxides having a phenyl group at the β-carbon showed a much higher reactivity with Me_2CuLi than other α,β-epoxy sulfoxides (Entries 6—8). 4) β-Disubstituted α,β-epoxy sulfoxide reacted very sluggishly with Me_2CuLi, giving enolate; however, the reaction of this enolate with benzaldehyde gave a complex mixture (Entry 9). 5) *threo*-Aldols were obtained exclusively or predominantly. 6) Acetone gave aldol in low yield (Entry 7). 7) In Entries 3, 8 and 4, 6, regioisomers of aldols (**16**, **5** and **17**, **19**, respectively) were synthesized in pure form; these results mean that these reactions are a kind of the directed aldol reaction.[3]

The possible mechanism of these reactions can be proposed as follows (Scheme 4). One electron transfer from Me_2CuLi to the α,β-epoxy sulfoxide **1** gives an anion radical intermediate **A**, which receives a second electron from Me_2CuLi to give a dianion intermediate **B**. Then elimination of the phenylsulfinyl group takes place to afford an enolate **C**. The enolate is trapped with electrophiles to give the product described in this paper. The stereochemistry of **C** in the aldol reaction is worth noting. Both isomers of the α,β-epoxy sulfoxides equally react with Me_2CuLi followed by aldehydes to afford *threo*-aldols. From these selectivities of the reaction, it can be presumed that the stereochemistry of the enolates is *E*, as shown in Scheme 4.[14]

Even though the reaction gave aldols with some limitation, we believe that the present method will prove to be valuable in the synthesis of aliphatic aldols with high regioselectivity.

Experimental

All melting points are uncorrected. The IR spectra were measured directly on a NaCl plate or KBr disks with a Hitachi 215 spectrometer. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with a JEOL FX-100 spectrometer or Hitachi R-24B spectrometer using Me_4Si as an internal standard. Electron-impact mass spectra (MS) were obtained on a Hitachi M-80 double-focusing spectrometer at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing a 2% fluoresence reagent (254) and a quartz column were used for column chromatography; products showing ultraviolet (UV) absorption were detected by UV



Scheme 4.

irradiation. Ether and THF were dried with benzophenone ketyl and distilled.

α,β-Epoxy Sulfoxides. All α,β-epoxy sulfoxides, except for **8** and the α,β-epoxy sulfoxide in Table 2 (Entry 3), were reported previously.[4,9] Two new α,β-epoxy sulfoxides were prepared from the aldehydes and 1-chloro-2-phenylethyl phenyl sulfoxide through chlorohydrins in the usual way.[4]

2,3-Epoxy-1-phenyl-2-phenylsulfinylpentane (Entry 3 in Table 2). *Z*-Isomer: Colorless semisolid, 44% overall yield. IR (neat): 1080 and 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.10 (3H, t, J=6 Hz), 1.99 (2H, m), 2.52 (1H, d, J=15 Hz), 2.62 (1H, t, J=6 Hz), 3.55 (1H, d, J=15 Hz), and 6.8—7.9 (10H, m); MS *m/z* (%) 286 (M$^+$, 0.5), 161 (9), 126 (13), and 91 (100); Found: *m/z* 286.1023. Calcd for $C_{17}H_{18}O_2S$: M, 286.1026. *E*-Isomer: Colorless oil, 40% overall yield. IR (neat): 1080 and 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.00 (3H, t, J=6 Hz), 1.58 (2H, m), 3.02 (2H, s), 3.68 (1H, t, J=6 Hz), and 6.8—7.9 (10H, m); MS *m/z* (%) 286 (M$^+$, 0.3), 161 (10), 126 (14), and 91 (100); Found: *m/z* 286.1017. Calcd for $C_{17}H_{18}O_2S$: M, 286.1025.

2,3-Epoxy-1-phenyl-2-phenylsulfinylnonane (8). *Z*-Isomer: Colorless oil, 43% overall yield. IR (neat): 1080 and 1050 (SO) cm^{-1}; ^{1}H NMR δ=0.90 (3H, t, J=6 Hz), 1.0—2.2 (10H, m), 2.53 (1H, d, J=15 Hz), 2.65 (1H, t, J=6 Hz), 3.58 (1H, d, J=15 Hz), and 6.7—7.9 (10H, m); MS *m/z* (%) 342 (M$^+$, trace), 217 (9), 126 (12), and 91 (100); Found: *m/z* 342.1655. Calcd for $C_{21}H_{26}O_2S$: M, 342.1653. *E*-Isomer: Colorless oil, 41% overall yield. IR (neat): 1080 and 1050 (SO) cm^{-1}; ^{1}H NMR δ=0.88 (3H, t, J=6 Hz), 1.0—1.7(10H, m), 3.04 (2H, s), 3.70 (1H, t, J=6 Hz), and 7.0—7.8 (10H, m); MS *m/z* (%) 342 (M$^+$, trace), 217 (9), 126 (11), and 91 (100); Found: *m/z* 342.1662. Calcd for $C_{21}H_{26}O_2S$: 342.1652.

1-Phenyl-2-pentanone (4). A solution of **3** (90 mg; 0.28 mmol) in 1 ml of dry ether was added to a solution of Me_2CuLi (0.56 mmol; prepared from MeLi and $CuBr\cdot SMe_2$ in ether at 0 °C) in ether (3 ml) at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 3 h; the reaction was then quenched with sat. aq. NH_4Cl. The solution was extracted with ether and the organic layer was washed with sat. aq. NH_4Cl. The usual work-up followed by silica-gel column chromatography afforded 35 mg (77%) of **4** as a colorless oil. IR (neat): 1710 (CO) cm^{-1}; ^{1}H NMR δ=0.96 (3H, t, J=7 Hz), 1.58 (2H, m), 2.41 (2H, t, J=7 Hz), 3.66 (2H, s), and 7.0—7.4 (5H, m); MS *m/z* (%) 162 (M$^+$, 18), 91 (48), and 71 (100); Found: *m/z* 163.1062. Calcd for $C_{11}H_{14}O$: M, 163.1076.

2-(*t*-Butyldimethylsiloxy)-1-phenyl-1-nonene (9). A solution of **7** (69 mg; 0.2mmol) in 1 ml of dry ether was added to a solution of Me_2CuLi (0.6 mmol) in 1.5 ml of ether at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 40 min. To the reaction mixture was added a solution of Et_3N (1 mmol) in 4 ml of dry THF followed by a solution of *t*-butyldimethylsilyl chloride (1 mmol) and HMPA (1 mmol) in 2 ml of THF. The solution was stirred at room temperature for 9 h. The reaction was quenched with H_2O and the whole was extracted with ether. The usual work-up followed by silica-gel column chromatography gave 60 mg (90%) of **9** (a mixture of E/Z=1/2) as a colorless oil. IR (neat): 1650 and 1255 cm^{-1}; ^{1}H NMR δ=−0.04, 0.00 (each 3H, s), 0.81 (9H, s), 0.7—1.0 (3H, m), 1.0—1.6 (12H, m), 2.08 (t, J=7 Hz, *E*-isomer), 2.32 (t, J=7 Hz, *Z*-isomer), 5.31 (s, vinyl-H, *Z*-isomer), 5.64 (s, vinyl-H, *E*-isomer), and 7.0—7.5 (5H, m); MS *m/z* (%) 332 (M$^+$, 25), 275 ([M−C_4H_9]$^+$, 100), and 191 (18); Found: *m/z* 332.2530. Calcd for $C_{21}H_{36}OSi$: M, 332.2527.

α,β-Epoxy sulfoxide **8** gave the same product on treatment with Me_2CuLi followed by *t*-butyldimethylsilyl chloride.

2-Acetoxy-3-phenyl-2-undecen-4-one (10). A solution of **7** (103 mg; 0.3 mmol) in 1 ml of ether was added to a solution of Me_2CuLi (0.9 mmol) in 2 ml of ether at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 30 min. To this reaction mixture was added acetyl chloride (3 mmol); the mixture was first stirred at 0 °C for 1.5 h and then at room temperature for 1 h. The reaction was quenched with 1% aq. ammonia and the whole was extracted with ether. The usual work-up followed by silica-gel column chromatography afforded 48 mg (53%) of **10** as a colorless oil. Single isomer; *E/Z* not determined. IR (neat): 1770 and 1700 (CO) cm^{-1}; ^{1}H NMR δ=0.85 (3H, t, J=6 Hz), 1.0—1.6 (10H, m), 1.92 (3H, s), 2.19 (2H, m), 2.21 (3H, s), and 7.1—7.5 (5H, m); MS *m/z* (%): 302 (M$^+$, 6), 260 ([M−C_2H_2O]$^+$, 19), 242 (20), 176 (71), 161 (92), and 43 (100); Found: *m/z* 302.1880. Calcd for $C_{19}H_{26}O_3$: M, 302.1880.

2-Acetoxy-3-hexyl-5-phenyl-2-penten-4-one (11). A similar treatment of **8** with Me_2CuLi followed by acetyl chloride gave **11** as a *E/Z*-mixture (1 : 1) in 30% yield. Colorless oil; IR (neat): 1760 and 1690 (CO) cm^{-1}; ^{1}H NMR δ=0.86 (3H, t, J=6 Hz), 1.0—1.6 (8H, m), 1.8—2.5 (8H, m), 3.76, 3.83 (each bs, 2H, $PhC\underline{H}_2CO$–), and 7.0—7.4 (5H, m); MS *m/z* (%) 302 (M$^+$, 1), 260 ([M−C_2H_2O]$^+$, 2), 211 ([M−$PhCH_2$]$^+$, 16), and 169 (100); Found: *m/z* 302.1904. Calcd for $C_{19}H_{26}O_3$: M, 302.1881.

2-Ethoxycarbonyloxy-1-phenylnonene (12). A solution of **7** (69 mg; 0.2 mmol) in 1 ml of ether was added to a solution of Me_2CuLi (0.6 mmol) in 1.5 ml of ether at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 30 min; then ethyl chloroformate (1 mmol) was added. The reaction mixture was stirred at 0 °C for 1.5 h; then the reaction was quenched with 1% aq. ammonia. The usual work-up followed by silica-gel column chromatography gave 30 mg (50%) of **12** (a mixture of *E/Z*; E/Z=2/1) as a colorles oil. IR (neat): 1765 (CO) and 1240 (COC) cm^{-1}; ^{1}H NMR δ=0.85 (3H, m, CH_3), 1.0—1.7 (13H, m), 2.28—2.60 (2H, m, $C{=}CC\underline{H}_2$), 4.0—4.2 (2H, m, $OC\underline{H}_2CH_3$), 5.90 (s, vinyl-H; Z), 6.33 (s, vinyl-H, E), and 7.0—7.5 (5H, m); MS *m/z* (%) 290 (M$^+$, 11), 218 ([M−$C_3H_4O_2$]$^+$, 21), 199 (15), 134 (43), and 91 (100); Found: *m/z* 290.1895. Calcd for $C_{18}H_{26}O_3$: M, 290.1881.

2-Ethoxycarbonyloxy-1-phenyl-2-nonene (13). A similar treatment of **8** with Me_2CuLi followed by ethyl chloroformate gave **13** as a *E/Z*-mixture (E/Z=3/2) in 81% yield. Colorless oil; IR (neat): 1760 (CO) and 1250 (COC) cm^{-1}; ^{1}H NMR δ=0.86 (3H, m, CH_3), 1.0—1.6 (11H, m), 1.6—2.1 (2H, m), 3.52 (3/5H, s, $PhC\underline{H}_2$), 3.85 (2/5H, s, $PhC\underline{H}_2$), 4.0—4.4 ($OC\underline{H}_2$–, and vinyl-H (*Z*), m), 4.95 (3/5H, t, J=7 Hz, vinyl-H (*E*)), and 7.0—7.6 (5H, m); MS *m/z* (%) 290 (M$^+$, 2), 207 (34), and 91 (100); Found: *m/z* 290.1893. Calcd for $C_{18}H_{26}O_3$: M, 290.1881.

General Procedure for the Preparation of Aldols from α,β-Epoxy Sulfoxides with Me_2CuLi Followed by Carbonyl Compounds: The synthesis of (1*R**,2*S**)-1-hydroxy-1,2-diphenyl-3-hexanone **5** from **3** is described. A solution of **3** (97 mg; 0.3 mmol) in 1 ml of ether was added to a solution of Me_2CuLi (0.9 mmol) in 2 ml of ether at 0 °C under N_2. The solution was stirred at 0 °C for 40 min. To this reaction mixture was added a solution of $ZnCl_2$ in ether (0.6 mmol) followed by benzaldehyde (0.33 mmol). The reaction mixture was stirred for 10 min; then the reaction was quenched with sat. aq. NH_4Cl. The solution was extracted with ether-benzene. The usual work-up followd by column chromatography gave 67 mg (74%) of **5** as colorless needles. Mp 48.5—50.5 °C (AcOEt-hexane); IR (KBr): 3400 (OH) and 1705 (CO) cm^{-1}; ^1H NMR δ=0.81 (3H, t, J=7 Hz), 1.56 (2H, sextet, J=7 Hz), 2.37 (2H, t, J=7 Hz), 3.93 (1H, d, J=9 Hz), 5.18 (1H, d, J=9 Hz), and 6.7—7.3 (10H, m); MS m/z (%) 250 ($[M-H_2O]^+$, 0.8), 207 (0.5), 162 (28), and 70 (100); Found: C, 80.62; H, 7.51%. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

4-Hydroxy-3-methyl-1,4-diphenyl-2-butanone (14). A threo/erythro (2/1) mixture; colorless oil; 80% yield. IR (neat): 3450 (OH) and 1720 (CO) cm^{-1}; ^1H NMR δ=0.88 (d, J=7 Hz threo), 1.07 (d, J=7 Hz, erythro), 2.8—3.2 (1H, m), 3.58 (s, $PhC\underline{H}_2$, erythro), 3.74 (s, $PhC\underline{H}_2$, threo), 4.69 (bd, J=9 Hz, threo), 4.90 (d, J=5 Hz, erythro), and 6.9—7.4 (10H, m); MS m/z (%): 254 (M^+, 4), 180 (6), 163 ($[M-PhCH_2]^+$, 17), 148 (44), and 107 (100); Found: m/z 254.1302. Calcd for $C_{17}H_{18}O_2$: M, 254.1305.

4-Hydroxy-3-methyl-1-phenyl-2-hexanone (15). A threo/erythro (2/1) mixture; colorless oil; 79% yield. IR (neat): 3475 (OH) and 1715 (CO) cm^{-1}; ^1H NMR δ=0.90 (3H, t, J=7 Hz), 1.12 (d, J=7 Hz, erythro), 1.13 (d, J=7 Hz, threo), 1.2—1.7 (2H, m), 2.5—2.9 (1H, m), 3.4—3.8 (1H, m), 3.77 (2H, s), and 7.0—7.4 (5H, m); MS m/z (%) 206 (M^+, 10), 148 ($[M-C_3H_6O]^+$, 13), 115 (72), and 91 (100); Found: m/z 206.1311. Calcd for $C_{13}H_{18}O_2$: M, 206.1305.

(3*R,4*S**)-3-Ethyl-4-hydroxy-1,4-diphenyl-2-butanone (16).** Colorless crystals; 53% yield; mp 59—60.5 °C (AcOEt-hexane). IR (KBr): 3405 (OH) and 1720 (CO) cm^{-1}; ^1H NMR δ=0.73 (3H, t, J=7 Hz), 1.1—1.8 (2H, m), 2.8—3.1 (1H, m), 3.63 (2H, s), 4.77 (1H, d, J=7 Hz), and 6.9—7.4 (10H, m); MS m/z (%) 268 (M^+, 2), 239 ($[M-C_2H_5]^+$, 1), 177 (22), 162 (25), and 91 (100); Found: C, 80.38; H, 7.51%. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

(3*R,4*S**)-3-Hexyl-4-hydroxy-1,4-diphenyl-2-butanone (17).** Colorless crystals; 60% yield; mp 62—63 °C (AcOEt-hexane). IR (KBr): 3400 (OH) and 1715 (CO) cm^{-1}; ^1H NMR δ=0.83 (3H, t, J=6 Hz), 0.9—1.8 (10H, m), 2.84—3.16 (1H, m), 3.61 (2H, s), 4.76 (1H, d, J=8 Hz), and 6.9—7.4 (10H, m); MS m/z (%) 324 (M^+, 0.6), 233 ($[M-PhCH_2]^+$, 6), 215 (4), 187 (8), and 127 (100); Found: C, 81.36; H, 8.77%. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.71%.

(3*R,4*S**)-4-Hydroxy-3-pentyl-1,4-diphenyl-2-butanone (18).** Colorless crystals; 74% yield; mp 70—71.5 °C (AcOEt-hexane). IR (KBr): 3400 (OH) and 1720 (CO) cm^{-1}; ^1H NMR δ=0.79 (3H, t, J=6 Hz), 0.9—1.8 (8H, m), 2.84—3.16 (1H, m), 3.61 (2H, s), 4.75 (1H, d, J=8 Hz), and 6.9—7.4 (10H, m); Ms m/z (%) 310 (M^+, 1), 219 ($[M-PhCH_2]^+$, 12), 173 (15), and 113 (100); Found: C, 81.17; H, 8.45%. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%.

(1*R,2*S**)-1-Hydroxy-1,2-diphenyl-3-decanone (19).** Colorless crystals; 70% yield; mp 55.5—57 °C (AcOEt-hexane). IR (KBr): 3400 (OH) and 1705 (CO) cm^{-1}; ^1H NMR δ=0.84 (3H, t, J=6 Hz), 0.9—1.7 (10H, m), 2.38 (2H, t, J=7 Hz), 3.93 (1H, d, J=9 Hz), 5.18 (1H, J=9 Hz), and 6.8—7.4 (10H, m); MS m/z (%) 306 ($[M-H_2O]^+$, 1), 218 ($[M-C_7H_6O]^+$, 23), 180 (13), 127 (80), and 57 (100); Found: C, 81.62; H, 8.81%. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.71%.

2-Hydroxy-2-methyl-3-phenyl-4-undecanone (20). Colorless oil; 52% yield. IR (neat): 3520 (OH) and 1700 (CO) cm^{-1}; ^1H NMR δ=0.84 (3H, t, J=6 Hz), 0.99 (3H, s), 1.0—1.8 (10H, m), 1.33 (3H, s), 2.36 (2H, t, J=7 Hz), 3.69 (1H, s), and 7.27 (5H, s); MS m/z (%) 216 ($[M-H_2O]^+$, 2), 218 ($[M-C_3H_6O]^+$, 98), and 127 ($[M-C_{10}H_{13}O]^+$, 100).

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References

1) α,β-Epoxy sulfoxides as useful itermediates in organic synthesis. 23. Part 22: T. Satoh, T. Sato, T. Oohara, and K. Yamakawa, *J. Org. Chem.*, in press.

2) J. March, "Advanced Organic Chemistry," 2 nd ed. McGraw-Hill Book Company, New York (1977); B. P. Mundy and M. G. Ellerd, "Name Reactions and Reagents in Organic Synthesis," John Wiley and Sons, New York (1988).

3) T. Mukaiyama, *Org. React.*, **28**, 228 (1982).

4) a) T. Satoh, Y. Kaneko, T. Izawa, K. Sakata, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **58**, 1983 (1985); b) T. Satoh, T. Kumagawa, and K. Yamakawa, *ibid.*, **58**, 2849 (1985); c) T. Satoh, Y. Kaneko, K. Sakata, and K. Yamakawa, *ibid.*, **59**, 457 (1986); d) T. Satoh, A. Sugimoto, K. Yamakawa, *Chem. Pharm. Bull.*, **35**, 4632 (1987); e) T. Satoh, K. Iwamoto, A. Sugimoto, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **61**, 2109 (1988) and references cited therein.

5) The preliminary communication of this study: T. Satoh, A. Sugimoto, M. Itoh, and K. Yamakawa, *Tetrahedron Lett.*, **30**, 1083 (1989).

6) R. W. Herr, D. M. Wieland, and C. R. Johnson, *J. Am. Chem. Soc.*, **92**, 3813 (1970); G. H. Posner, *Org. React.*, **22**, 253 (1975); J. P. Marino and D. M. Floyd, *Tetrahedron Lett.*, **1979**, 675; A. Alexakis, G. Cahiez, and J. F. Normant, *Tetrahedron*, **36**, 1961 (1980); A. Ghribi, A. Alexakis, and J. F. Normant, *Tetrahedron Lett.*, **25**, 3075 (1984); B. H. Lipshutz, R. S. Wilhelm, J. A. Kozlowski, and D. Parker, *J. Org. Chem.*, **49**, 3928 (1984); J. M. Chong and K. B. Sharpless, *Tetrahedron Lett.*, **26**, 4683 (1985).

7) H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976); E. C. Ashby and D. Coleman, *J. Org. Chem.*, **52**, 4554 (1987).

8) K. Tamao, E. Nakajo, and Y. Ito, *J. Org. Chem.*, **53**, 414 (1988).

9) T. Satoh, A. Sugimoto, and K. Yamakawa, *Chem. Pharm. Bull.*, **37**, 184 (1989).

10) H. O. House, C-Y. Chu, J. M. Wilkins, and M. J. Umen, *J. Org. Chem.*, **40**, 1460 (1975).

11) Both *E*- and *Z*-isomer of the α,β-epoxy sulfoxides **3** showed the same reactivity with Me_2CuLi.

12) a) H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, **95**, 3310 (1973); b) K. K. Heng and R. A. J. Smith, *Tetrahedron*, **35**, 425 (1979).

13) R. Baker, J. L. Castro, and C. J. Swain, *Tetrahedron Lett.*, **29**, 2247 (1988).

14) W. Carruthers, "Some Modern Methods of Organic Synthesis," 3rd ed., pp. 48—63, Cambridge University Press, Cambridge (1986).