Stereoselective Epoxidation of Allylic Alcohols and Dehydrogenative Oxidation of Secondary Alcohols by Means of *t*-Butyl Hydroperoxide and Aluminium Reagents

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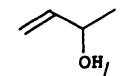
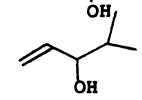
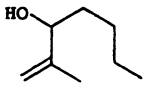
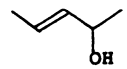
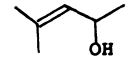
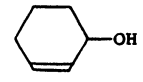
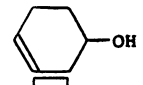
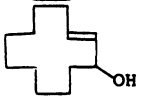
Treatment of a solution of geraniol and $(t\text{-BuO})_3Al$ in benzene with *t*-BuOOH at 5 °C gives (2*R**, 3*R**)-2,3-epoxy-3,7-dimethyl-6-octenyl acetate in 83% yield after acetylative workup. Eight allylic alcohols are converted to α,β-epoxy alcohols in preparative yields. The epoxidation of secondary (*E*)-allylic alcohols shows opposite stereoselectivities to *t*-BuOOH–$VO(acac)_2$ system. Asymmetric epoxidation with a chiral hydroxamic acid as a ligand gives unsatisfactory degrees of enantiomeric excess. The same system can also convert secondary alcohols into ketones in excellent yields, while primary ones react very slowly.

The versatility of the epoxide functionality in synthesis makes further advances in stereoselective acyclic epoxidation to be of particular interest.[1] Conventional oxidation with organic peracids[2] or epoxidation with *t*-butyl hydroperoxide in the presence of transition metal catalysts,[3,4] for example, $VO(acac)_2$, $Mo(CO)_6$, and $Ti(OPr^i)_4$, is suitable for such purpose.[5] We wish to report that *t*-BuOOH–$(t\text{-BuO})_3Al$ system effects stereoselective epoxidation of allylic alcohols as well as dehydrogenative oxidation of secondary alcohols to ketones.[6]

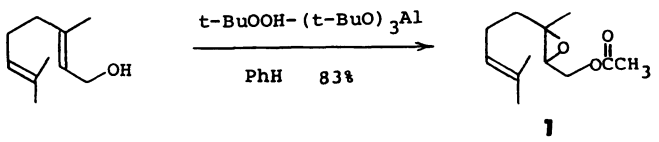
Trialkylaluminium compounds interact energetically with alkyl hydroperoxides to form organoaluminium peroxides.[7] The utility of these products as an oxidizing reagent, however, has been limited[8] because of their instability. They can react with the host trialkylaluminium compounds themselves or alternatively undergo intramolecular rearrangement.[9] We have found that the organoaluminium peroxide prepared *in situ* from *t*-BuOOH and $(t\text{-BuO})_3Al$ has proved to be effective for the title oxidation.[10]

Treatment of a solution of geraniol and $(t\text{-BuO})_3Al$ in benzene with *t*-BuOOH at 5 °C gave (2*R**, 3*R**)-2,3-epoxy-3,7-dimethyl-6-octenyl acetate (**1**) in 83% yield

TABLE 1. EPOXIDATION OF OLEFINIC ALCOHOLS WITH *t*-BuOOH–$(t\text{-BuO})_3Al$[a]

Run	Alcohol	Reaction conditions		Yield[b] %	Product		*t*-BuOOH–$VO(acac)_2$[d]	
		Temp/°C	Time/h		*threo*[c] (*trans*) (%)	*erythro*[c] (*cis*) (%)	*threo* (*trans*) (%)	*erythro* (*cis*) (%)
1		25	5	70	42	58	20	80
2		25	4	78	71	29	15	85
3		25	6	80	13	87	2	98
4		5	6	78	64	36	29	71
5		5	4	80	>99.5	<0.5	86	14
6		5	3	72	<0.5	>99.5	2	98
7		5	3	82	<0.5	>99.5	2	98
8		5	10	80	83	17	29	71[e]

a) All reactions were performed in benzene solution containing the substrates (2.0 mmol), $(t\text{-BuO})_3Al$ (3.0 mmol), and *t*-BuOOH (4.0 mmol). b) Isolated yields are underlined, all others are by GLPC relative to internal standard. Epoxy alcohols were acetylated *in situ* prior to analysis in Runs 5, 6, and 7. c) The resulting mixtures of epoxy alcohols, epoxy acetates, or epoxy alcohol trimethylsilyl ethers were analyzed by GLPC. d) Cited from Ref. 4a. e) Cited from Ref. 21.

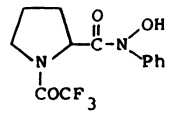


Scheme 1.

after acetylative workup (Scheme 1). Epoxidation of 6,7-olefinic linkage was not observed analogously as the *t*-BuOOH–VO(acac)$_2$ oxidation.

The results are shown in Table 1, together with the recorded selectivity of the Sharpless' *t*-BuOOH–VO(acac)$_2$ oxidation for comparison.[4a] Cyclohexenols with *Z*-configuration were preferentialy oxidized to cis epoxide by both methods commonly (Runs 6 and 7). The striking difference, however, has been observed in Runs 2, 4, and 8. The present aluminium reagent converted (*E*)-allylic alcohols predominantly into threo isomers which are less favored products in the vanadium one.

Asymmetric epoxidation[11] was examined with a chiral hydroxamic acid (**2**) as a ligand. A chiral aluminium reagent was prepared by treating trimethylaluminium with 1.2 equiv of **2** in benzene and used *in situ*. Epoxidation of geraniol with *t*-BuOOH and the reagent gave **1** in 34% e.e., whereas the reaction of 2,3-diphenyl-2-propen-1-ol gave **3** in 38% e.e.



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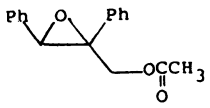

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The Oppennauer oxidation employing aluminium as a key atom is one of the useful methods for mild oxidation.[12] Recently Posner has reported selective oxidation of alcohols by means of Al_2O_3–Cl_3CCHO system.[13] The present system has provided another means of oxidizing secondary alcohols into corresponding ketones with excellent yields as shown in Table 2. Allylic secondary alcohols gave epoxy ketones in one pot (Runs 5 and 6).

Meanwhile, primary alcohols, such as 1-dodecanol reacted much more slowly[14] and required prolonged period (2 d) afford a complex mixture which contained dodecanal (13% yield) and 1-dodecanol (54% recovery). Under the conditions described for the oxidation of secondary alcohols, many functional groups were inert. For example, 1-iododododecane, methyl dodecanoate, phenylacetylene, anisole, and dodecanal diethylene acetal were recovered unchanged in 95, 95, 98, 98, and 86% yields, respectively, after exposure to the oxidant.

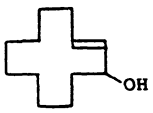
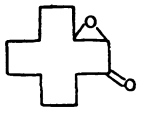
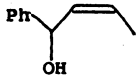
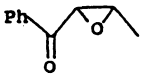
Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer; the mass spectra, on a Hitachi M-80 machine; and the NMR spectra, on a Varian EM-360 spectrometer. The chemical shifts are given in δ, with TMS as the internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Benzene was dried on sodium and distilled. *t*-Butyl hydroperoxide (70% aqueous solution) was purchased from Nakarai and used without further purification. All the experiments were carried out under an argon atmosphere. Purification of products were performed by preparative thin layer chromatography (TLC) or column chromatography on silica gel (Merck Kieselgel 60). Analytical GLPC was performed with a Yanagimoto GCG-550-F or Shimadzu GC-4CPT. Preparative GLPC was performed with a JEOL-JGC-20K apparatus.

The *threo/erythro* nomenclature for the relative configuration of two adjacent asymmetric centers of α,β-epoxy alcohols was determined according to the Noyori's formalism.[15]

Epoxidation of Allylic Alcohols by Means of t-*BuOOH–(*t-*BuO)$_3$-Al Reagent.* *t*-Butyl hydroperoxide (70%, 0.51 g, 4.0 mmol) was added at 5 °C (or 25 °C) to a stirred solution of an allylic alcohol (2.0 mmol) and (*t*-BuO)$_3$Al (0.74 g, 3.0 mmol) in benzene (10 ml). The resulting mixture was stirred at this temperature for an appropriate time described in Table 1. The reaction mixture was acetylated *in situ* for the entry 5, 6, and 7 by treating with acetic anhydride (1.02 g, 10 mmol) and pyridine (0.79 g, 10 mmol) at 25 °C for 1 h. The whole was

TABLE 2. OXIDATION OF SECONDARY ALCOHOLS WITH *t*-BuOOH–(*t*-BuO)$_3$Al

Run	Alcohol	Reaction conditions[a] Temp/°C	Time/h	Product	Yield[b] %
1	$PhCH(OH)CH_3$	25	6	$PhCOCH_3$	90
2	Cyclododecanol	25	18	Cyclododecanone	85
3	2-Octanol	25	12	2-Octanone	(100)
4	4-*t*-Butylcyclohexanol	25	15	4-*t*-Butylcyclohexanone	85
5		80[c]	6		47
6		80[c]	9		48

a) Reactions were performed in benzene solutions (10 ml) containing the substrates (2.0 mmol), (*t*-BuO)$_3$Al (3.0 mmol), and *t*-BuOOH (4.0 mmol). b) Except the case of 2-octanol where yield was determined by GLPC, all yields were isolated ones. c) *t*-BuOOH (8.0 mmol) and (*t*-BuO)$_3$Al (5.0 mmol) were used.

diluted with ether (10 ml), poured into 1 M †hydrochloric acid (20 ml), and extracted with ether. The organic layer was washed with aq $NaHSO_3$ (15 ml), aq $NaHCO_3$ (20 ml), and brine (2×20 ml), dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate) or preparative GLPC.

(2R, 3R*)-2,3-Epoxy-3,7-dimethyl-6-octenyl Acetate (1).*[4a] Bp 94 °C (bath temp, 1 Torr, 1 Torr=133.322 Pa); IR (neat): 2940, 2350, 1750, 1460, 1375, 1230, 1038 cm^{-1}; NMR (CCl_4): δ=1.27 (s, 3H), 1.03—2.40 (m, 4H), 1.60 (s, 3H), 1.66 (s, 3H), 2.03 (s, 3H), 2.77 (t, J=6 Hz, 1H), 3.77—4.27 (m, 2H), 5.00 (bt, J=7 Hz, 1H); MS *m/e* (%): 212 (M^+, 1), 134 (11), 109 (74), 82 (31), 69 (50), 43 (100).

Conversion of threo- *and* erythro-*1,2-Epoxy-3-butanol*[16] *to* threo- *and* erythro-*2,3-Octanediol Acetonide.* This procedure was used to determine the ratio of *threo* and *erythro* epoxides produced by the oxidation of 3-buten-2-ol, because the separation of the diastereomeric epoxy alcohols by GLPC was not ideal.

Copper(I) iodide (12 g, 60 mmol) was suspended in anhydrous ether (150 ml). To this cooled (−20 °C) and stirred suspension was added butyllithium (1.7 M solution in hexane, 71 ml, 0.12 mol) dropwise over a period of 1 h. The mixture was allowed to stir for an additional 30 min, and then an etheral solution (30 ml) of a mixture of *threo*- and *erythro*-1,2-epoxy-3-butanols (approximately 7.5 mmol) was added at −20 °C. The whole was allowed to warm to 0 °C over a period of 1 h. The mixture was quenched by cautiously adding a sat. ammonium chloride solution. The copper salts were filtered off and the organic layer was washed twice with brine (40 ml), dried over anhydrous $MgSO_4$ and concentrated. The crude mixture of the diols was dissolved in acetone (10 ml). Perchloric acid (70%, 4 drops) was added to this and the resulting mixture was stirred at 25 °C for 1 h. The reaction mixture was quenched with 20% sodium hydroxide (2 ml) and extracted three times with hexane. The organic layer was separated and subjected to GLPC analysis (3% OV-17, 2 m, 65 °C) to show two peaks, T_r=6.2 min (*threo*-isomer, 42%) and T_r=8.7 min (*erythro*-isomer, 58%). *threo*-2,3-Octanediol acetonide: Bp 52 °C (bath temp, 3 Torr); IR (neat): 2948, 2880, 1464, 1382, 1248, 1180, 1100, 862 cm^{-1}; NMR (CCl_4): δ=0.90 (bt, J=6 Hz, 3H), 1.14 (d, J=6 Hz, 3H), 1.27 (s, 6H), 1.15—1.58 (m, 8H), 3.20—3.70 (m, 2H); MS *m/e* (%): 171 (M^+-CH_3, 100), 111 (18), 86 (56), 69 (74), 59 (32); Found: C, 70.89; H, 12.11%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%. *erythro*-2,3-Octanediol acetonide: Bp 60 °C (bath temp, 3 Torr); IR (neat): 2940, 2860, 1460, 1376, 1240, 1215, 1080, 855 cm^{-1}; NMR (CCl_4): δ=0.92 (bt, J=6 Hz, 3H), 1.05 (d, J=6 Hz, 3H), 1.22 (s, 6H), 1.00—1.62 (m, 8H), 3.75—4.18 (m, 2H); MS *m/e* (%): 171 (M^+-CH_3, 49), 129 (25), 86 (44), 69 (100), 59 (54); Found: C, 71.07; H, 12.09%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%.

threo- *and* erythro-*1,2-Epoxy-4-methyl-3-pentanol.*[16] The crude product was treated with *N*-(trimethylsilyl)imidazole (1.1 equiv) in dichloromethane. GLPC analysis (20%, PEG 6000, 2 m, 80 °C) of the resulting trimethylsilyl ethers indicated two peaks, T_r=7.8 min (*threo*-isomer, 71%) and T_r=7.0 min (*erythro*-isomer, 29%), which could not separated completely. The analytically pure samples of both isomers were prepared by preparative GLPC (20% PEG 6000). *threo*-Alcohol trimethylsilyl ether: Bp 67 °C (bath temp, 25 Torr); IR (neat): 2960, 1248, 1085, 928, 836 cm^{-1}; NMR ($CDCl_3$): δ=0.13 (s, 9H), 0.92 (d, J=6 Hz, 3H), 0.95 (d, J=6 Hz, 1H), 1.79 (dqq, J=5, 6, 6 Hz, 1H), 2.55—2.59 (m, 1H), 2.81 —2.83 (m, 1H), 2.91—2.93 (m, 2H); MS *m/e* (%): 173 (M^+-CH_3, 33), 145 (100), 75 (59), 73 (58). *erythro*-Alcohol trimethylsilyl ether: Bp 68 °C (bath temp. 25 Torr); IR (neat): 2970, 1472, 1250, 1068, 875, 838 cm^{-1}; NMR ($CDCl_3$): δ=0.13 (s, 9H), 0.92 (d, J=6 Hz, 3H), 0.95 (d, J=6 Hz, 3H), 1.79 (dqq, J=5, 6, 6 Hz, 1H), 2.61—2.72 (m, 2H), 2.85—2.95 (m, 1H), 3.34 —3.41 (m, 1H); MS *m/e* (%): 173 (M^+-CH_3, 4), 145 (63), 81 (10), 75 (45), 73 (100).

threo- *and* erythro-*1,2-Epoxy-2-methyl-3-heptanol.*[17] TLC (CH_2Cl_2–ether, 5 : 1) of the product derived from epoxidation of 2-methyl-1-hepten-3-ol indicated two spots, R_f=0.33 (*threo*-isomer, 13%) and R_f=0.43 (*erythro*-isomer, 87%). The *threo*/*erythro* isomer ratio was determined by GLPC (5% PEG 20M, 2 m, 85 °C), which showed two peaks at 26.0 min (*threo*-isomer) and at 15.0 min (*erythro*-isomer). The analytically pure samples of both isomers were prepared by preparative TLC. *threo*-Isomer: Bp 80 °C (bath temp, 1 Torr); IR (neat): 3450, 2940, 1460, 1050, 900, 874 cm^{-1}; NMR (CCl_4): δ=0.80—1.03 (bt, J=6 Hz, 3H), 1.27 (s, 3H), 1.15—1.55 (m, 6H), 2.15 (bs, 1H), 2.49 (d, J=5 Hz, 1H), 2.63 (d, J=5 Hz, 1H), 3.00—3.30 (m, 1H); MS *m/e* (%): 129 (M^+-CH_3, 1), 101 (11), 87 (16), 72 (40), 71 (87), 69 (37), 58 (100). *erythro*-Isomer: Bp 80 °C (bath temp, 1 Torr); IR (neat): 3460, 2960, 2940, 1460, 900, 788 cm^{-1}; NMR (CCl_4): δ=0.82—1.06 (bt, J=6 Hz, 3H), 1.06—1.78 (m, 6H), 1.28 (s, 3H), 2.00 (bs, 1H), 2.45 (d, J=5 Hz, 1H), 2.76 (d, J=5 Hz, 1H), 3.42—3.60 (m, 1H); MS *m/e* (%): 129 (M^+-CH_3, 1), 101 (9), 72 (28), 71 (70), 69 (32), 58 (100).

threo- *and* erythro-*(3R*, 4R*)-3,4-Epoxy-2-pentanol.*[18] Treatment of the crude epoxides derived from (*E*)-3-penten-2-ol with *N*-(trimethylsilyl)imidazole (1.1 equiv) in dichloromethane gave the trimethylsilyl ethers, which were analyzed by GLPC (10% PEG 20M, 2 m, 70 °C). GLPC indicated two peaks, T_r=7.8 min (*threo*-isomer, 64%) and T_r=6.6 min (*erythro*-isomer, 36%). The analytically pure samples were prepared by preparative GLPC (20% PEG 20M). *threo*-Alcohol trimethylsilyl ether: Bp 54 °C (bath temp, 13 Torr); IR (neat): 2960, 1450, 1370, 1248, 1098, 1052, 1012, 954, 890, 838, 750 cm^{-1}; NMR ($CDCl_3$): δ=0.12 (s, 9H), 1.19 (d, J=6 Hz, 3H), 1.30 (d, J=4 Hz, 3H), 2.64 (dd, J=2, 6 Hz, 1H), 2.85 (dq, J=2, 6 Hz, 1H), 3.56 (dq, J=6, 6 Hz, 1H); MS *m/e* (%): 159 (M^+-CH_3, 53), 117 (80), 115 (100), 73 (94). *erythro*-Alcohol trimethylsilyl ether: Bp 56 °C (bath temp, 12 Torr); IR (neat): 2960, 1450, 1370, 1248, 1094, 1004, 892, 836, 775 cm^{-1}; NMR ($CDCl_3$): δ=0.10 (s, 9H), 1.22 (d, J=6 Hz, 3H), 1.29 (d, J=5 Hz, 3H), 2.58 (dd, J=2, 5 Hz, 1H), 2.90 (dq, J=2, 5 Hz, 1H), 3.59 (dq, J=6, 6 Hz, 1H); MS *m/e* (%): 159 (M^+-CH_3, 50), 117 (92), 115 (100), 73 (84).

threo-*3,4-Epoxy-4-methyl-2-pentanol.*[18] GLPC analysis (5% PEG 20M, 2 m, 65 °C) showed that the product was homogeneous, having a retention time of 13.6 min: *threo*-Isomer: Bp 75 °C (bath temp, 15 Torr); IR (neat): 3450, 2970, 1720, 1378, 1112, 1070, 1030, 890, 868, 805 cm^{-1}; NMR (CCl_4): δ=1.16 (d, J=6 Hz, 3H), 1.28 (s, 3H), 1.30 (s, 3H), 2.57 (d, J=7 Hz, 1H), 3.33 (bs, 1H), 3.53 (dq, J=7, 6 Hz, 1H); MS *m/e* (%): 116 (M^+, trace), 72 (6), 59 (100), 58 (33), 57 (38), 45 (31).

Cf. erythro-Isomer:[18] Bp 76 °C (bath temp, 15 Torr); T_r= 19.1 min (5% PEG 20M, 2 m, 65 °C); IR (neat): 3450, 2970, 1645, 1380, 1112, 946, 906, 790 cm^{-1}; NMR (CCl_4): δ=1.25 (d, J=6 Hz, 3H), 1.27 (s, 3H), 1.30 (s, 3H), 1.55 (bs, 1H), 2.42 (d, J=7 Hz, 1H), 3.57 (dq, J=7, 6 Hz, 1H); MS *m/e* (%): 101 (M^+-CH_3, 1), 72 (6), 59 (100), 58 (27), 57 (33), 45 (34).

cis-*2,3-Epoxy-1-cyclohexanol.*[19] Bp 88 °C (bath temp, 18 Torr); IR (neat): 3300, 2950, 1650, 1420, 1058, 938, 846 cm^{-1}; NMR (CCl_4): δ=1.03—2.25 (m, 7H), 3.03—3.33 (m, 2H), 3.63—4.10 (m, 1H); MS *m/e* (%): 114 (M^+, 3), 96 (20),

† 1 M=1 mol dm^{-3}.

70 (100), 68 (32), 67 (48), 57 (96).

A small aliquot was acetylated with acetic anhydride and pyridine. GLPC analysis (10% PEG 20M, 2 m, 125 °C) indicated a peak (T_r=12.4 min) due to the *cis*-epoxy acetate. A peak at 9.8 min, corresponding to the *trans*-isomer prepared independently,[19] was absent.

cis-*3,4-Epoxy-1-cyclohexanol.*[20] Bp 79 °C (bath temp, 16 Torr); IR (neat): 3370, 2950, 1670, 1440, 1260, 1065, 990, 818, 792 cm^{-1}; NMR (CCl_4): δ=1.00—2.35 (m, 7H), 2.96—3.12 (m, 2H), 3.40—3.78 (m, 1H); MS *m/e* (%): 114 (M^+, trace), 95 (5), 71 (44), 70 (94), 57 (56), 42 (100).

After acetylation, the *cis/trans* isomer ratio was determined by GLPC (3% Silicone OV-17, 2 m, 75 °C), which indicated one peak at 40 min corresponding to the *cis*-epoxy acetate. The absence of *trans*-isomer[20] (T_r=36 min) was confirmed by the comparison with the authentic sample.

cis- *and* trans-*2,3-Epoxycyclododecanol.*[21] The two isomers were separated by column chromatography (hexane–ether, 5 : 1) on silica gel. *cis*-Isomer: Bp 81 °C (bath temp, 0.1 Torr); R_f=0.43 (hexane–ether, 1 : 1); IR (neat): 3350, 2950, 1462, 1448, 912, 870, 674 cm^{-1}; NMR (CCl_4): δ=0.97—2.27 (m, 19H), 2.72 (t, J=2 Hz, 1H), 2.90 (dt, J=10, 2 Hz, 1H), 3.85—4.08 (m, 1H); MS *m/e* (%): 198 (M^+, trace), 121 (24), 111 (38), 98 (52), 95 (67), 82 (83), 81 (87), 67 (65), 57 (100). *trans*-Isomer: Bp 83 °C (bath temp, 0.1 Torr); R_f=0.23 (hexane–ether, 1 : 1); IR (neat): 3450, 2950, 1475, 1465, 1040, 896, 788 cm^{-1}; NMR (CCl_4): δ=0.93—2.32 (m, 18H), 2.63 (bs, 1H), 2.53—2.88 (m, 2H), 2.90—3.18 (m, 1H); MS *m/e* (%): 198 (M^+, trace), 121 (17), 111 (28), 98 (41), 95 (59), 82 (71), 81 (72), 57 (100).

Asymmetric Epoxidation of Allylic Alcohols with a Chiral Aluminium Compound and t-*BuOOH.* The chiral ligand **2** was prepared by acylation of *N*-phenylhydroxylamine with *N*-trifluoroacetyl-(*S*)-prolyl chloride according to the literature.[22] **2**: $[\alpha]_D^{25}$ −61.3 (*c* 1.5, acetone). To a stirred solution of trimethylaluminium (1.0 M solution in hexane, 3.0 ml, 3.0 mmol) in benzene (15 ml) was added at 25 °C a benzene solution of **2** (1.1 g, 3.6 mmol) and the whole was stirred at the same temperature for 1 h. Then allylic alcohol (2.0 mmol) and *t*-butyl hydroperoxide (70%, 0.51 g, 4.0 mmol) were added successively and the resulting mixture was heated to reflux for an additional 3 h. After acetylation and a usual workup as mentioned before, the crude product was purified by preparative TLC.

1: $[\alpha]_D^{25}$ −8.6 (*c* 1.5, acetone). **3**: $[\alpha]_D^{25}$ −16.7 (*c* 0.6, CCl_4). Enantiomeric excess of these products were also checked by NMR with Eu(hfc)$_3$ shift reagent.

(2R, 3R*)-2,3-Epoxy-2,3-diphenylpropyl Acetate (3).*[11c] Mp 42.0 °C (hexane); IR (KBr): 1748, 1504, 1454, 1220, 1035, 745, 695 cm^{-1}; NMR (CCl_4): δ=1.98 (s, 3H), 4.16 (s, 1H), 4.23 (d, J=12 Hz, 1H), 4.50 (d, J=12 Hz, 1H), 6.80—7.20 (m, 10H); MS *m/e* (%): 225 (M^+−$COCH_3$, 1), 167 (10), 162 (28), 120 (100), 107 (38), 103 (26), 43 (48); Found: C, 75.98; H, 6.00%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

Oxidation of Secondary Alcohols by Means of t-*BuOOH–(*t-*BuO)$_3$Al Reagent.* To a stirred solution of a secondary alcohol (2.0 mmol) and (*t*-BuO)$_3$Al (0.74 g, 3.0 mmol) in benzene (10 ml) was added at 25 °C a benzene solution of *t*-BuOOH (0.44 g, 4.0 mmol). The resulting mixture was stirred at 25 °C for an appropriate time described in Table 2. The mixture was diluted with ether (10 ml) and poured into 1 M hydrochloric acid (20 ml). The separated organic layer and ether extracts were washed with aq $NaHSO_3$ (15 ml), aq $NaHCO_3$ (20 ml), and brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography (hexane–ethyl acetate) on silica gel (20 g).

The yield of 2-octanone was determined by GLPC (10% PEG 20M, 2 m, 50 °C) using dodecane as the internal standard.

Preparation of α,β-Epoxy Ketones by Means of t-*BuOOH–(*t-*BuO)$_3$Al Reagent.* A solution of an allylic secondary alcohol (2.0 mmol) and (*t*-BuO)$_3$Al (1.2 g, 5.0 mmol) in benzene (10 ml) was treated with a benzene solution of *t*-butyl hydroperoxide (70%, 1.0 g, 8.0 mmol) at 80 °C for 6 (9) h. After a usual workup, the crude product was purified by column chromatography (hexane–ethyl acetate) on silica gel (20 g).

(2R, 3R*)-2,3-Epoxycyclododecanone.* Mp 42.5 °C (hexane); IR (CCl_4): 2930, 1722, 1465, 1428 cm^{-1}; NMR (CCl_4): δ=0.95—1.93 (m, 15H), 1.95—2.40 (m, 2H), 2.63—3.00 (m, 2H), 3.30 (d, J=1.5 Hz, 1H); MS *m/e* (%): 196 (M^+, 4), 153 (12), 111 (53), 98 (92), 84 (90), 55 (100); Found: *m/e* 196.1464. Calcd for $C_{12}H_{20}O_2$: M, 196.1464.

(2R, 3S*)-2,3-Epoxy-1-phenyl-1-butanone.* Bp 123 °C (bath temp, 1 Torr); IR (neat): 2960, 1698, 1602, 1588, 1456, 1412, 1230, 940, 702 cm^{-1}; NMR (CCl_4): δ=1.16 (d, J=5 Hz, 3H), 3.32 (dq, J=5, 5 Hz, 1H), 3.97 (d, J=5 Hz, 1H), 7.15—7.63 (m, 3H), 7.83—8.15 (m, 2H); MS *m/e* (%): 162 (M^+, 12), 147 (8), 105 (100), 77 (35); Found: *m/e* 162.0704. Calcd for $C_{10}H_{10}O_2$: M, 162.0681.

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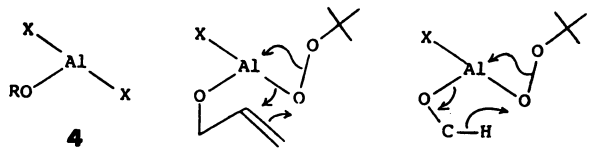
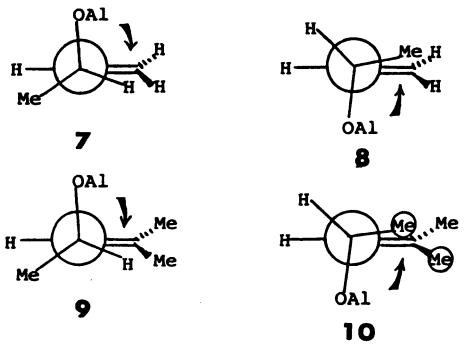


4 **5** **6**

X = *t*-BuO or Me

BuOOH (or the evolution of methane gas (Me_3Al)) to provide the product **4**. Successive addition of *t*-BuOOH affords the intermediate **5** or **6** in which the peroxide bond is polarized by a three centered interaction with an empty coordination site on the aluminium atom. The O–O bond is cleaved by π-electron of the suitably situated double bond (for the epoxidation of allylic alcohols) **5** or by hydride uptake (for the oxidation of secondary alcohols) **6** to afford the corresponding product. There has been considerable interest in establishing optimum O–C–C–C dihedral angles for epoxidation of allylic alcohols with both peracid[18,20] and vanadium catalysts.[4a,21,23] The *threo*/*erythro* ratios with *t*-BuOOH–$(t\text{-BuO})_3$Al system are rather close to those with peracid epoxidation and a dihedral angle near 120° seems to fit our data. The preferred conformations are illustrated in Scheme 2 for the epoxidation of allylic alcohols (Runs 1 and 5 in Table 1). The conformer **10** is much less favorable as compared to **9** due to the severe steric interaction between two Me group circled. No such remarkable steric interaction can be seen in the former case (**7** and **8**).



7 **8** **9** **10**

Scheme 2.

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