# Lewis Base-Catalyzed Addition of Trialkylaluminum Compounds to Epoxides

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**Keywords:** Catalysis / Epoxides / Lewis bases / Aluminum

A novel concept for catalytic epoxide alkylation has been developed. Lewis bases like phosphanes, arsanes, stibanes, and sulfides were found to catalyze the alkylation of symmetrical epoxides with trialkylaluminum compounds very effectively at a 5 mol % level. Cyclic as well as acyclic epoxides were readily alkylated in good yields. In reactions with terminal epoxides a significant enhancement of rate and/or regioselectivity was noted in the Lewis base-catalyzed process. Coordination of the Lewis base to the Lewis acidic aluminum reagent was proved by $^{27}Al$ and $^{31}P$ NMR spectroscopy and is proposed to form a more nucleophilic alkylating agent.

## Introduction

Epoxides are valuable fine chemicals and synthetic intermediates. As such, a great deal of attention has been paid to their chemo-, diastereo- and enantioselective preparation by epoxidation of the corresponding alkenes.[1] The synthetic importance of epoxides stems in large part from their facile and *trans*-stereospecific nucleophilic ring opening with all kinds of nucleophiles to furnish valuable amino alcohols,[2] azido alcohols,[3] halohydrins,[4] diols,[5] and thiols[6] to name the most frequently prepared addition products.

Among the carbon nucleophiles that successfully alkylate epoxides are organolithium compounds in concert with various activating agents,[7] such as organomagnesium,[8] organocopper,[9] organozinc[10] and organolanthanide reagents.[11] A conceptually different approach uses $Ti^{III}$ reagents, which upon single-electron transfer generate radical anions from the epoxides which may be trapped with olefins to accomplish the C−C bond forming process.[12] Trialkylaluminum compounds usually do not alkylate epoxides[13] unless they are either coordinated to the substrate prior to the reaction[14] or specially activated by organolithium compounds, metal alkoxides, or water which presumably form more reactive aluminum "ate" complexes.[15]

We report here a novel approach to catalyze the addition of trialkylaluminum compounds to epoxides. Stimulated by the powerful amine catalysis in diethylzinc additions to aldehydes[16] we envisioned the activation of trialkylaluminum compounds with catalytic quantities of Lewis bases to effect the epoxide opening. Principally, coordination of a Lewis base to the Lewis acid $R_3Al$ should result in the formation of a tetracoordinate aluminum complex which resembles the above mentioned "ate" complexes and which should exhibit a comparable reactivity towards the epoxides.

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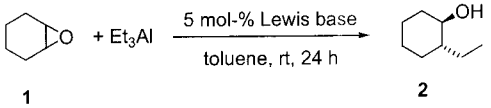
## Results and Discussion

We selected the reaction of cyclohexene oxide (**1**) with $Et_3Al$ as our model reaction and screened a broad range of Lewis bases to evaluate their catalytic activity (Table 1).[17] Toluene was chosen as a noncoordinating solvent to avoid interactions with the aluminum reagent.

Phosphanes, arsanes, stibanes, and sulfides were identified as suitable catalysts at a 5 mol % level in toluene at room temperature to give the ring-opened product, *trans*-2-ethyl-1-cyclohexanol (**2**), in typically excellent yields. Ethers and amines turned out to be totally ineffective as catalysts. Stoichiometric amounts of the aluminum reagent were sufficient for a complete reaction but the reaction rate was greatly enhanced employing two equivalents of $Et_3Al$. Without the Lewis base present the reaction did not proceed at all. The exclusive formation of the *trans*-addition product was indicative of a stereospecific reaction path via a concerted nucleophilic displacement mechanism.

The alkylation of cyclohexene oxide (**1**) could be extended to the reaction with $Me_3Al$. Some differences in the catalytic activity exist, however. Here sulfides no longer catalyze the alkyl transfer efficiently and triphenylstibane was

Table 1. Lewis base-catalyzed reaction of cyclohexene oxide (**1**) with $Et_3Al$ (1 equiv.)




**1** **2**

| Entry | Lewis base | Yield (%)[a] |
|---|---|---|
| 1 | – | 0 |
| 2 | $NEt_3$ | 0 |
| 3 | $Et_2O$ | 0 |
| 4 | $PBu_3$ | 89 |
| 5 | $PPh_3$ | 99 |
| 6 | $P(NMe_2)_3$ | 97 |
| 7 | $AsPh_3$ | 100 |
| 8 | $SbPh_3$ | 89 |
| 9 | $Me_2S$ | 100 |

[a] Determined by GC.

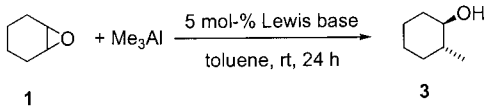
  1434−193X/01/1223−4445 $ 17.50+.50/0 

shown to be the most active catalyst along with triphenylarsane and tris(dimethylamino)phosphane, furnishing the addition product *trans*-2-methyl-1-cyclohexanol (**3**), again in very good yields (Table 2). Triphenylarsane was selected as our standard Lewis base catalyst for the subsequent studies on disubstituted epoxides as it has the broadest scope and applicability.

Cyclic and acyclic epoxides were readily alkylated with either $Me_3Al$ or $Et_3Al$ according to the general protocol giving rise to the alkylated products in typically good isolated yields (Table 3). The alkylation of the more unreactive cyclopentene oxide (**4**) was conducted at 50 °C to achieve a good product yield within 24 h. The diastereomeric *cis*- and *trans*-2-butene oxides (**5**) and (**6**), respectively, were alkylated with $Et_3Al$ to yield the *anti*-product **11** from **5** and the *syn*-product **12** from **6**, exclusively, proving a strictly stereospecific reaction course. The rather moderate yields observed in these reactions are presumably due to the volatility of the products during their isolation. Accordingly, the reaction with $Me_3Al$ was not attempted here.

The uncatalyzed addition of $Et_3Al$ to *cis*-stilbene oxide (**7**) gave rise to a product mixture consisting mainly of the rearranged product **16** and none of the desired product **13** (Figure 1). The $AsPh_3$-catalyzed nucleophilic addition of either trialkylaluminum reagent to **7**, however, cleanly furnished the ring-opened products **13** and **14**, respectively, in good yields. On the other hand. however, the reaction of *trans*-stilbene oxide (**8**) with $Et_3Al$ even under Lewis base catalysis yielded a mixture of the two diastereomeric 1,2-diphenyl-1-butanols (**13**) and (**15**) along with the rearranged product **16** in roughly equal amounts. Two conclusions may be drawn from this observation. Apparently, the phenyl ring adjacent to the epoxide provides sufficient resonance stabilization for the formation of a putative carbenium ion, shifting the mechanism of the epoxide alkylation towards a two-step process. Secondly, the substrate configuration plays a critical role in determining whether this change in mechanism actually occurs.

Table 2. Lewis base-catalyzed reaction of cyclohexene oxide (**1**) with $Me_3Al$ (1 equiv.)

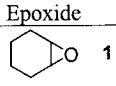
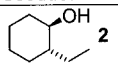
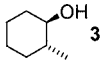
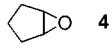
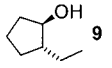
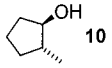
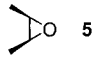
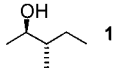
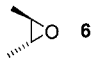
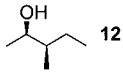
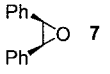
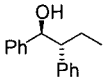
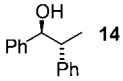
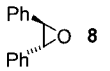
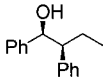



**1** **3**

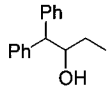
| Entry | Lewis base | Yield (%)[a] |
|---|---|---|
| 1 | – | 2 |
| 2 | $PPh_3$ | 81 |
| 3 | $P(NMe_2)_3$ | 90 |
| 4 | $AsPh_3$ | 87 |
| 5 | $SbPh_3$ | 99 |
| 6 | $Me_2S$ | 3 |

[a] Determined by GC.

Table 3. $AsPh_3$-catalyzed (5 mol %) addition of $Et_3Al$ and $Me_3Al$ (1 equiv.) to symmetrical epoxides (toluene, room temp., 24 h)

| Entry | Epoxide | $R_3Al$ | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 |  **1** | $Et_3Al$ |  **2** | 94 |
| 2 | **1** | $Me_3Al$ |  **3** | 82 |
| 3 |  **4** | $Et_3Al$[b] |  **9** | 75 |
| 4 | **4** | $Me_3Al$[b] |  **10** | 70 |
| 5 |  **5** | $Et_3Al$ |  **11** | 62 |
| 6 |  **6** | $Et_3Al$ |  **12** | 59 |
| 7 |  **7** | $Et_3Al$ |  **13** | 79 |
| 8 | **7** | $Me_3Al$ |  **14** | 71 |
| 9 |  **8** | $Et_3Al$ |  **15 (+ 13 + 16)** | 76[c] |

[a] Isolated yields of chromatographed product. – [b] Reaction conducted at 50°C. – [c] 1:1:1 Mixture of **15**, **13** and **16**.




**16**

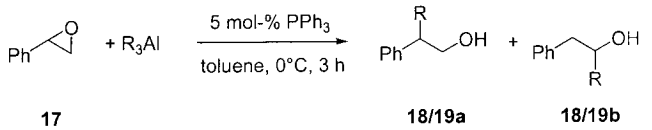
Figure 1. Unwanted side product from the reaction of *trans*-stilbene oxide and $Et_3Al$

We noted, however, some limitations in this newly developed process. Cyclooctene oxide, a notoriously unreactive epoxide, could not be alkylated using this method. Not unexpectedly, reactions with higher trialkylaluminum compounds, such as triisobutylaluminum, with the epoxides resulted in β-hydride transfer furnishing the corresponding alcohols.

We also investigated the alkylation of terminal epoxides with trialkylaluminum compounds, which proceeds even in the absence of a Lewis base. The regioselectivity, however, was significantly affected in the presence of catalytic quantities of a Lewis base. Thus, styrene oxide (**17**) was alkylated with $Et_3Al$ and $Me_3Al$ with high regioselectivity at the internal position to furnish **18a** and **19a**, respectively, in excellent yields in the presence of 5 mol % of $PPh_3$. On the other hand, the uncatalyzed reaction furnished substantial amounts of the regioisomers **18b** and **19b**, which were presumably formed through an epoxide opening-hydride migration-alkylation sequence (Table 4). The opposite regioselectivity is reported in reactions of styrene oxide with higher-order cyanocuprates, which are the most popular organometallics employed in epoxide alkylations,[9c] whereas one has to resort to diorganomagnesium reagents to find the same regioselectivity as in our study.[9f] Thus, our results

obtained with trialkylaluminum/Lewis base combinations constitute a useful addition to current synthetic methodology.

Table 4. $PPh_3$-catalyzed (5 mol %) addition of $Et_3Al$ and $Me_3Al$ to styrene oxide (**17**)

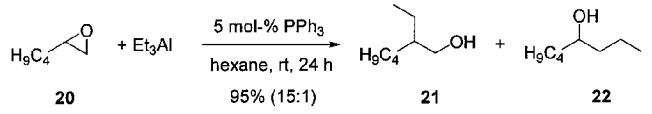



**17** **18/19a** **18/19b**

| Entry | $R_3Al$ | Lewis base | Ratio **a/b** | Major Product | Yield [%][a] |
|---|---|---|---|---|---|
| 1 | $Et_3Al$ | -- | 2/1 | **18a** | 75 |
| 2 | $Et_3Al$ | $PPh_3$ | 50/1 | **18a** | 95 |
| 3 | $Me_3Al$ | -- | 3/1 | **19a** | 90 |
| 4 | $Me_3Al$ | $PPh_3$ | 24/1 | **19a** | 92 |

[a] Combined yield of both isomers after chromatographic purification.

A significant rate enhancement was noted in the reaction of triethylaluminum with 1-hexene oxide (**20**) under Lewis base catalysis (Scheme 1). Without the Lewis base present the addition products **21** and **22** were obtained in 58% combined yield with a regioselectivity of 15:1 in favor of the internal addition product **21**. In the presence of 5 mol % of $PPh_3$, however, the reaction proceeded almost to completion within 24 h at room temp. giving rise to a 95% yield of the same regioisomeric composition.



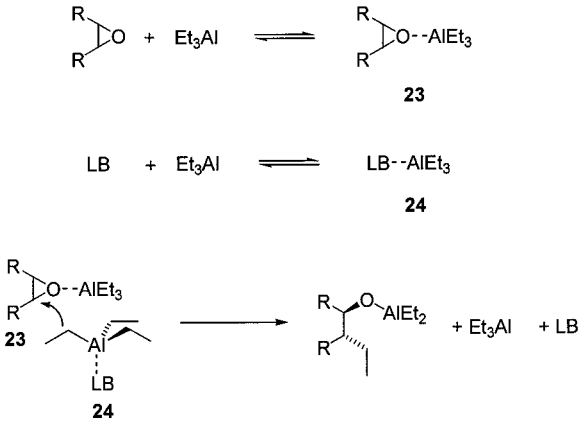

**20** **21** **22**

Scheme 1

## Mechanistic Considerations

Trimethylaluminum and triethylaluminum are known to form dimers in hydrocarbon solution that are in equilibrium with small quantities of the monomeric species.[18] When the epoxide is added to the solution of the aluminum reagent in toluene it will certainly − as a Lewis base itself − coordinate to the Lewis acidic aluminum reagent to form a monomeric trialkylaluminum-epoxide complex **23** (Scheme 2). Once the catalytic Lewis base is added to the reaction mixture it competes with the epoxide for coordination to the aluminum reagent.

We were able to show by NMR spectroscopy that coordination of a phosphane to triethylaluminum actually occurs. Mixing equimolar quantities of triethylaluminum and tris(dimethylamino)phosphane results in a downfield shift in the $^{27}Al$ NMR spectrum from $\delta = 155$ (for $Et_3Al$ alone) to $\delta = 165$ (for a 1:1 mixture of $Et_3Al$ and the phosphane), suggesting the formation of a monomeric tetracoordinate aluminum species.[19] An even more significant upfield shift from $\delta = 123$ to $\delta = 97$ was observed in the $^{31}P$ NMR spectrum.




Scheme 2

As long as $R_3Al$ is employed in excess (2 equiv.) the competition between the epoxide and the catalytic Lewis base poses no problem and the trialkylaluminum-Lewis base complex **24** should form easily (Scheme 2). If the trialkylaluminum reagent is employed only stoichiometrically, however, **24** will form in significantly lower concentrations because the epoxide, as a hard Lewis base, coordinates to the hard Lewis acidic aluminum center more effectively. These two complexes **23** and **24** are presumed to effect the alkylation of the epoxide, with one equivalent of the trialkylaluminum reagent serving as a Lewis acid to activate the epoxide and the second equivalent of the trialkylaluminum reagent coordinated by the catalytic Lewis base delivering the alkyl group in a nucleophilic sense. Such a transition structure with two trialkylaluminum compounds participating in the transition structure has already been suggested for the reaction of trimethylaluminum and benzophenone.[20]

Although we have not undertaken a systematic kinetic investigation we observed a significant rate increase in the $PPh_3$-catalyzed (5 mol %) reaction of $Et_3Al$ and cyclohexene oxide (**1**) when using two equivalents as opposed to one equivalent of the aluminum reagent. When we monitored the conversion as a function of time we noted that half of the substrate was consumed within only 80 min at room temperature when using two equivalents $Et_3Al$ whereas the half-time was 5 h in the reaction with only 1 equivalent of $Et_3Al$ under otherwise identical reaction conditions.

The origin of rate enhancement in the Lewis base-catalyzed reaction may be electronic and/or steric. The bonds to the attached carbon ligands are likely to be weakened due to electron donation from the Lewis base to the electron-deficient aluminum atom. This same effect has previously been observed in other Lewis base-catalyzed organometallic reactions, most notably in the amine-catalyzed addition of dialkylzinc compounds to aldehydes,[16] the *N*,*N*-dimethylformamide-catalyzed addition of allyltrichlorosilanes to aldehydes,[21] the phosphoramide-catalyzed aldol reaction of trichlorosilyl enolates,[22] the amine- and phosphane-catalyzed addition of trimethylsilyl cyanide to aldehydes,[23] and the phosphane-catalyzed aldol reaction of ke-

tene silyl acetals.[24] A weakening of the Al−C bonds may also, however, be caused by compression of the binding angle around the aluminum atom upon coordination of the bulky Lewis base.

## Conclusion

We have devised a novel strategy to catalyze the addition of trialkylaluminum compounds to epoxides. Only 5 mol % of a soft Lewis base was employed to effect the methylation and ethylation of cyclic and acyclic epoxides. The epoxide-opening reaction was shown to proceed stereospecifically in all but one cases to furnish the *trans*-addition products exclusively. Aside from the rate enhancement, which was also observed in reactions with other electrophiles,[17] a significant increase of rate and/or regioselectivity was noted in the alkylation of styrene oxide and 1-hexene oxide. Spectroscopic evidence suggests a coordination of the Lewis base to the aluminum atom which apparently results in the formation of a more nucleophilic alkylating agent.

## Experimental Section

**General:** All reactions were carried out under $N_2$ using flame-dried glassware. Solvents were distilled from the appropriate drying agents immediately prior to use. All reactions were monitored by gas chromatography using a Varian Star 3400 CX instrument, a BP1 column of SGE (50m × 0.25 mm) and hydrogen (22 psi) as carrier gas. $^1$H and $^{13}$C NMR: Varian VXR 200 (200 MHz), Bruker AMX 300 (300 MHz) and Varian VXR 500 (500 MHz) with tetramethylsilane as internal standard. $^{27}$Al NMR: Bruker AM 250 (65.2 MHz) with $AlCl_3$ as external standard. $^{31}$P NMR: Bruker Avance 500 (162 MHz) with $H_3PO_4$ as external standard. IR: Bruker IFS 25 FT-IR. MS: Finnigan MAT 95A. Column chromatography was performed on silica gel (0.063−0.200 mm) from Macherey−Nagel & Co.

**General Protocol for the Addition of Trialkylaluminum Compounds to Epoxides:** 0.15 mmol of the Lewis base was added to a solution of 3.00 mmol epoxide in 6 mL dry toluene and subsequently 3.00 mmol of the respective trialkylaluminum compound was added as a solution in either hexane or toluene. The mixture was stirred for 24 h at room temp. or 50 °C under a nitrogen atmosphere, cooled to −78 °C and then quenched with 5 mL of a 1 M HCl solution. The phases were separated and the aqueous layer was extracted twice with ether. The combined organic extracts were dried over $MgSO_4$ and the solvents evaporated in vacuo. The crude products were purified by flash chromatography over silica gel with ether/pentane mixtures. The yields given in Table 1 and 2 were determined by GC on the crude products with *n*-decane as internal standard and with use of a calibrated curve. The yields given in Table 3 and 4 and in the Exp. Sect. are isolated yields of chromatographed and analytically pure material.

***trans*-2-Ethyl-1-cyclohexanol (2):**[25] Yield: 360 mg (94%). $t_R$ = 7.57 min (100 °C, 10 min, 20 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.5 Hz, 3 H, $CH_3$), 1.04−1.42 (m, 6 H), 1.61−2.02 (m, 6 H), 3.23 (dt, *J* = 4.5, 9.5 Hz, 1 H, 1-H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ = 10.8, 24.6, 25.0, 25.6, 29.5, 35.7, 46.5, 74.4. IR (film): $\tilde{\nu}$ = 3345 cm$^{-1}$ (O−H), 2961, 2929, 2858 (C−H), 1045 (C−O). EI-MS (70 eV): *m*/*z* = 128 (5) [$M^+$], 110 (72) [$M^+ - H_2O$], 57 (100) [$C_4H_9^+$].

***trans*-2-Methyl-1-cyclohexanol (3):**[25] Yield: 280 mg (82%). $t_R$ = 4.98 min (100 °C, 10 min, 20 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.5 Hz, 3 H, $CH_3$), 1.12−1.40 (m, 5 H), 1.55−2.02 (m, 5 H), 3.12 (dt, *J* = 4.5, 9.5 Hz, 1 H, 1-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 18.6, 25.2, 25.7, 33.6, 35.5, 40.3, 76.5. IR (film): $\tilde{\nu}$ = 3419 cm$^{-1}$ (O−H), 2930, 2858 (C−H), 1090 (C−O). EI-MS (70 eV): *m*/*z* = 114 (20) [$M^+$], 96 (60) [$M^+ - H_2O$], 81 (62), 68 (69), 57 (100) [$C_4H_9^+$].

***trans*-2-Ethyl-1-cyclopentanol (9):**[26] Yield: 257 mg (75%). $t_R$ = 4.94 min (50 °C, 2.5 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.10−1.28 (m, 2 H), 1.45−2.00 (m, 8 H), 3.83 (q, *J* = 6.0 Hz, 1 H, 1-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 12.6, 21.9, 26.6, 29.6, 34.7, 50.0, 78.9. IR (film): $\tilde{\nu}$ = 3346 cm$^{-1}$ (O−H), 2958, 2874 (C−H), 1092 (C−O). EI-MS (70 eV): *m*/*z* = 114 (18) [$M^+$], 96 (52) [$M^+ - H_2O$], 81 (57), 68 (62), 57 (100) [$C_4H_9^+$].

***trans*-2-Methyl-1-cyclopentanol (10):**[26] Yield: 210 mg (70%). $t_R$ = 3.65 min (50 °C, 2.5 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.16 (mc, 1 H), 1.42−1.80 (m, 5 H), 1.90 (mc, 2 H), 3.74 (q, *J* = 6.0 Hz, 1 H, 1-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 18.2, 21.5, 31.6, 34.1, 42.7, 80.6. IR (film): $\tilde{\nu}$ = 3348 cm$^{-1}$ (O−H), 2956, 2872 (C−H), 1080 (C−O). EI-MS (70 eV): *m*/*z* = 100 (10) [$M^+$], 82 (39) [$M^+ - H_2O$], 81 (57), 57 (100) [$C_4H_9^+$].

***anti*-2-Hydroxy-3-methylpentane (11):**[27] Yield: 190 mg (62%). $t_R$ = 6.32 min (50 °C, 4 min, 10 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.0 Hz, 3 H, $CH_3$), 0.90 (t, *J* = 6.5 Hz, 3 H, $CH_3$), 1.12 (d, *J* = 6.0 Hz, 3 H, $CH_3$), 1.35−1.58 (m, 4 H), 3.67 (quint, *J* = 6.0 Hz, 1 H, 2-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 11.6, 14.1, 19.4, 25.2, 41.8, 71.5. IR (film): $\tilde{\nu}$ = 3362 cm$^{-1}$ (O−H), 2966, 2933, 2878 (C−H), 1100 (C−O). DCI-MS (70 eV): *m*/*z* = 120 (100) [$M + NH_4^+$].

***syn*-2-Hydroxy-3-methylpentane (12):**[27] Yield: 180 mg (59%). $t_R$ = 6.19 min (50 °C, 4 min, 10 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.0 Hz, 3 H, $CH_3$), 0.91 (t, *J* = 6.5 Hz, 3 H, $CH_3$), 1.15 (d, *J* = 6.0 Hz, 3 H, $CH_3$), 1.27−1.58 (m, 4 H), 3.70 (mc, 1 H, 2-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 11.8, 13.8, 20.3, 25.3, 41.6, 71.2. IR (film): $\tilde{\nu}$ = 3356 cm$^{-1}$ (O−H), 2964, 2878 (C−H), 1078 (C−O). DCI-MS (70 eV): *m*/*z* = 120 (100) [$M + NH_4^+$].

***anti*-1,2-Diphenyl-1-butanol (13):**[28] Yield: 535 mg (79%). $t_R$ = 15.68 min (100 °C, 6 min, 20 °C/min). $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.75 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.57 (br. s, 1 H, OH), 1.75 (mc, 1 H, C*H*$_2$), 1.98 (mc, 1 H, C*H*$_2$), 2.84 (ddd, *J* = 10.5, 6.0, 4.0 Hz, 1 H, 2-H), 4.80 (d, *J* = 6.0 Hz, 1 H, 1-H), 7.00−7.25 (m, 10 H, phenyl-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 12.1, 22.7, 55.5, 78.4, 126.3, 126.5, 127.1, 127.9, 128.0, 128.9, 141.3, 143.0. IR (film): $\tilde{\nu}$ = 3403 cm$^{-1}$ (O−H), 2963, 2930, 2874 (C−H), 1025 (C−O). EI-MS (70 eV): *m*/*z* = 226 (2) [$M^+$], 120 (100) [$M^+$ − PhCHOH], 107 (96) [$PhCHOH^+ + 1$].

***anti*-1,2-Diphenyl-1-propanol (14):**[29] Yield: 450 mg (71%). $t_R$ = 15.24 min (100 °C, 6 min, 20 °C/min). $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 6.0 Hz, 3 H, $CH_3$), 1.84 (br. s, 1 H, OH), 3.11 (quint, *J* = 6.0 Hz, 1 H, 2-H), 4.82 (d, *J* = 6.0 Hz, 1 H, 1-H), 7.10−7.25 (m, 10 H, phenyl-H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 14.9, 47.2, 78.7, 126.3, 126.4, 127.1, 127.9, 128.0, 128.2, 142.8, 143.5. IR (film): $\tilde{\nu}$ = 3395 cm$^{-1}$ (O−H), 2960, 2928, 2871 (C−H), 1015 (C−O). EI-MS (70 eV): *m*/*z* = 212 (6) [$M^+$], 106 (100) [$M^+$ − PhCHOH], 107 (96) [$PhCHOH^+ + 1$].

***syn*-1,2-Diphenyl-1-butanol (15):**[28] Yield: 515 mg (76%) of a 1:1:1-mixture of **13**, **15**, and **16** were obtained in the reaction of *trans*-stilbene oxide (**8**) with $Et_3Al$ and 5 mol % of $AsPh_3$ according to the general procedure. Data for **15**: $t_R$ = 15.45 min (100 °C, 6 min, 20 °C/min). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.63 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.42−1.64 (m, 2 H, $CH_2$), 1.67 (br. s, 1 H, OH), 2.75 (ddd, *J* = 12.0, 8.0, 4.0 Hz, 1 H, 2-H), 4.72 (d, *J* = 8.0 Hz, 1 H, 1-H), 7.00−7.25 (m, 10 H, phenyl-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 11.9, 24.9, 56.1, 78.3, 126.4, 126.7, 127.1, 127.8, 128.1, 128.9, 141.1, 143.0.

**1,1-Diphenyl-2-butanol (16):**[30] $t_R$ = 15.78 min (100 °C, 6 min, 20 °C/min). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.30−1.48 (m, 2 H, $CH_2$), 1.67 (br. s, 1 H, OH), 3.90 (d, *J* = 7.5 Hz, 1 H, 1-H), 4.29 (dt, *J* = 3.0, 7.5 Hz, 1 H, 2-H), 7.00−7.25 (m, 10 H, phenyl-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 10.1, 27.8, 58.3, 75.0, 126.3, 126.5, 127.1, 127.9, 128.0, 128.9, 141.3, 143.0.

**2-Phenyl-1-butanol (18a):**[31] Yield: 400 mg (89%) of a 50:1 regioisomeric mixture. $t_R$ = 11.93 min (100 °C, 6 min, 10 °C/min), regioisomer: $t_R$ = 11.47 min. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.50 (br. s, 1 H, OH), 1.55−1.83 (m, 2 H, 3-H), 2.68 (mc, 1 H, 2-H), 3.71 (dd, *J* = 10.0, 7.5 Hz, 1 H, 1-H), 3.76 (d, *J* = 10.0, 6.0 Hz, 1 H, 1-H), 7.20−7.38 (m, 5 H, phenyl-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 12.0, 25.0, 50.5, 67.3, 126.6, 128.1, 128.6, 142.2. IR (film): $\tilde{\nu}$ = 3361 $cm^{-1}$ (O−H), 2962, 2929, 2874 (C−H), 1453, 1037 (C−O). DCI-MS (70 eV): *m*/*z* = 168 (100) [M + $NH_4^+$].

**2-Phenyl-1-propanol (19a):**[32] Yield: 330 mg (81%) of a 24:1 regioisomeric mixture. $t_R$ = 10.27 min (100 °C, 6 min, 10 °C/min), regioisomer: $t_R$ = 9.33 min. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 7.0 Hz, 3 H, $CH_3$), 1.58 (br. s, 1 H, OH), 3.05 (sext, *J* = 7.0 Hz, 1 H, 2-H), 3.80 (d, *J* = 7.0 Hz, 2 H, 1-H), 7.25−7.34 (m, 5 H, phenyl-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.6, 42.4, 68.7, 126.7, 127.5, 128.6, 143.7. IR (film): $\tilde{\nu}$ = 3354 $cm^{-1}$ (O−H), 2962, 2929, 2874 (C−H), 1583, 1091, 1068 (C−O). EI-MS (70 eV): *m*/*z* = 136 (9) [$M^+$], 105 (100) [$M^+ - CH_2OH$], 77 (16) [$Ph^+$].

**2-Ethyl-1-hexanol (21):**[33] Yield: 360 mg (95%) of a 15:1 regioisomeric mixture. $t_R$ = 6.24 min (50 °C, 2 °C/min). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.90 (2 × t, *J* = 7.0 Hz, 6 H, $CH_3$), 1.20−1.58 (m, 10 H), 3.50 (dd, *J* = 11.0, 6.0 Hz, 1 H, 1-H), 3.54 (dd, *J* = 11.0, 5.0 Hz, 1 H, 1-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 11.1, 14.1, 23.2, 23.4, 29.1, 30.2, 42.0, 65.1. IR (film): $\tilde{\nu}\tilde{\gamma}$ = 3346 $cm^{-1}$ (O−H), 2958, 2930, 2872 (C−H), 1013 (C−O). DCI-MS (70 eV): *m*/*z* = 144 (100) [M + $NH_4^+$].

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