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Titanocene-Promoted Eliminations on Epoxy Alcohols and Epoxy Esters

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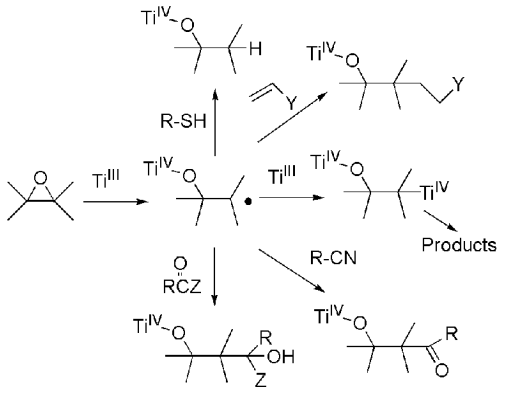
The reaction of a series of 2,3-epoxy alcohols and the corresponding formates, acetates, and benzoates promoted by Cp_2TiCl has been studied. The different outcome of the reaction of epoxy derivatives has been rationalized in terms of mechanistically biased processes. After homolytic oxirane cleavage, four main types of reaction were found: dehydroxylation, decarboxylation, dehydrogenation, and deoxygenation. The reaction products varied according to the substitution pattern. The radical nature of these eliminations is demonstrated.

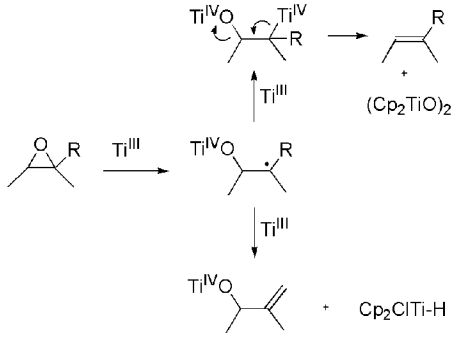
Introduction

Epoxides are a convenient source of functionalized radicals. The method based on the titanocene-mediated opening of epoxides through single-electron transfer introduced by Nugent and RajanBabu,[1] and the catalytic version developed by Gansäuer et al.,[2] have been the object of many interesting applications in synthesis.[3] The radicals, generated by the reaction of epoxides with paramagnetic Cp_2TiCl (Scheme 1), can be trapped, in both intramolecular and intermolecular addition reactions, by acceptors such as hydrogen,[1–3] alkenes,[1–3] carbonyls,[4] and nitriles.[5] In a second way, the radicals could be reduced by Ti^{III} to an alkyltitanium complex.[1–3]



Scheme 1. Addition reactions induced by titanocene on epoxides.

It has been shown that in the absence of radical acceptors 1,2-disubstituted epoxides (Scheme 2, R = H) can be deoxygenated by treatment with Cp_2TiCl. This deoxygenation has been explained in terms of homolytic cleavage of the oxirane, followed by reduction of the secondary incipient radical with Ti^{III} and further anionic β-elimination.[6]



Scheme 2. Reactions of disubstituted and trisubstituted epoxides.

We also found that trisubstituted epoxides, with at least a methyl substituent (Scheme 2, R = Me) give allylic alcohols through the elimination of a hydrogen atom instead of deoxygenation.[4a,7] This dehydrogenation method has been applied to the synthesis of a variety of *exo*-methylene allylic alcohols from epoxy carvone derivatives.[8]

The different kinds of behavior of trisubstituted epoxides with respect to disubstituted ones would be due to the incipient tertiary radical, which is sterically hindered in comparison with the secondary radicals. The methyl hydrogen atoms of these intermediates are more accessible for the Ti^{III} organometallic reagent.[4a,9]

Regarding this issue, a new type of selective elimination of a hydroxy group has been provided by Yadav et al.[10] from the reaction of 2,3-epoxy primary alcohols with Cp_2TiCl. The proposed mechanism (Scheme 3) consists of

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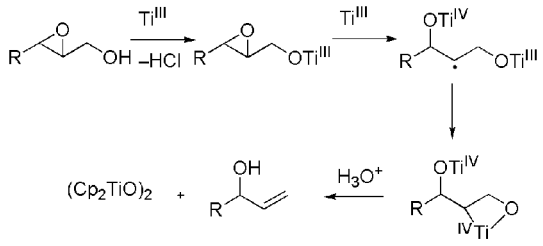
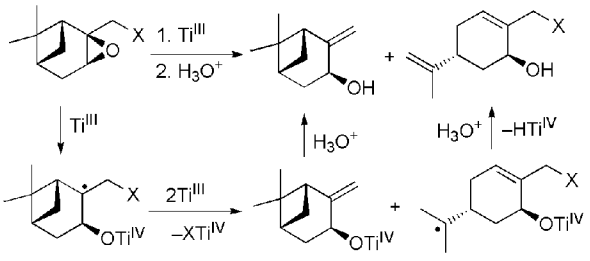
the formation of Ti^{III}–alkoxide, as an initial step, followed by homolytic oxirane cleavage to afford the incipient radical, which subsequently participates intramolecularly with the unfilled d orbital of Ti^{III} to form an oxetane intermediate, which then evolves into an alkene and titanocene oxide.



Scheme 3. Dehydroxylation of 2,3-epoxy alcohols with Ti^{III}.

Two related selective eliminations of formyloxyl and acetoxyl groups from the formates and acetates of the 2,3-epoxy primary alcohols have been found by our group.[4c] Also, a β-scission of CN from β,γ-epoxy nitriles has been reported recently.[9b] The kinetics of all these fragmentations corresponds to radical reactions, as we have demonstrated with our radical clock based on pinene derivatives (Scheme 4).[11]

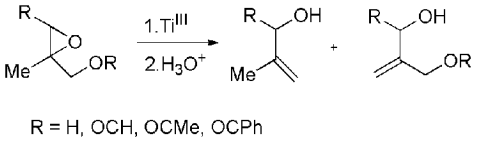


Scheme 4. Elimination radical clocks.

The selective β-fragmentation mediated by titanocene chloride would be a powerful route to allylic alcohols. Taking the reactions described above as a starting point, here we investigated the mechanism, kinetics, and scope of those elimination reactions. To the best of our knowledge, little attention has been devoted to this topic,[12] apart from the few papers reported above.

Results and Discussion

Here we report our findings on the reactions between functionalized epoxides and titanocene chloride (Scheme 5).

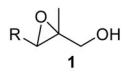
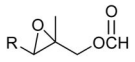
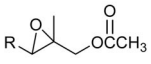
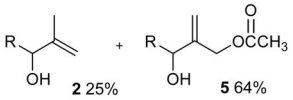
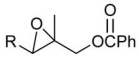
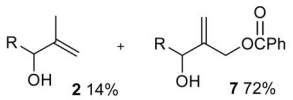
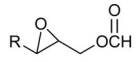
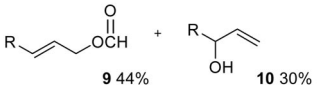
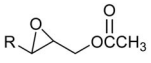
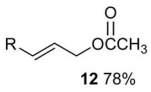


Scheme 5. Eliminations induced by titanocene.

Reactions were carried out by adding two equivalents of titanocene dichloride to one equivalent of the functionalized epoxide in tetrahydrofuran at room temperature. The regiochemical outcome of the cleavage reaction is in agreement with what has been observed previously with nonsymmetrical oxiranes.[13] Epoxide opening is directed by nonbonding interactions during electron transfer. In almost all cases, the formation of allylic alcohols was observed.

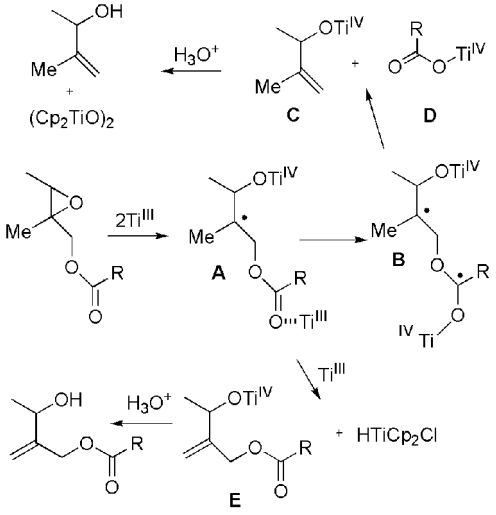
We carried out the work with a series of acyclic epoxy alcohols and epoxy esters, which were prepared by known procedures from heptanal. The first series of primary alcohol **1** and its derived esters and related compounds is summarized in Table 1.

Table 1. Cp_2TiCl-induced eliminations on epoxy alcohol **1** and its esters.

Entry	Epoxide (R = *n*-hexyl)	Products and Yield
1	 **1**	 **2** 85%
2	 **3**	 **2** 83%
3	 **4**	 **2** 25% **5** 64%
4	 **6**	 **2** 14% **7** 72%
5	 **8**	 **9** 44% **10** 30%
6	 **11**	 **12** 78%

The reaction of titanocene chloride with epoxy alcohol **1** and epoxy formate **3** afforded exclusively allylic alcohol **2** in good yield. The first result is in agreement with previous experiments reported by Yadav[10] with 1,2-disubstituted epoxides. Unlike formate **3**, the reaction of acetate **4** and benzoate **6** provided a mixture of alcohol **2** and hydroxy esters **5** and **7**, respectively, in different ratios. In both cases, the major product resulted from β-hydrogen elimination. The evolution of the disubstituted epoxides was different: whereas epoxy formate **8** gave deoxygenation and deformylation products, **9** and **10**, epoxy acetate **11** only gave deoxygenation product **12**. A tentative graphical explanation of the results shown in Table 1 is given in Scheme 6.

The eliminations induced by titanocene chloride took place following several competitive pathways (Schemes 3 and 6). The mechanism proposed by Yadav[10] (Scheme 3) explains the behavior of epoxy alcohol **1**. In the reaction of epoxy formate **3** (Scheme 6, R = H) the initial step would be the well-documented titanocene-mediated opening of epoxides, which afforded β-alkoxy radical **A**. In this interme-



Scheme 6. Elimination pathways.

diate, the carbonyl group must be coordinated to Ti^{III} and further evolves to diradical **B**, which undergoes β-fragmentation to give **C** and **D**. The hydrolysis step finally provided the allylic alcohol and the titanocene oxide.

For epoxy esters **4** and **6**, an alternative pathway from radical **A** would also operate; that is, the transfer of a hydrogen from the methyl group[4a,7,9] to Cp_2TiCl to give **E**. The subsequent hydrolysis afforded the corresponding unsaturated hydroxy ester.

It is worth noting that hydrogen elimination is faster than decarboxylation on epoxy esters **4** and **6**. The rate of ester elimination decreased from formate **3** to benzoate **6** and this is consistent with the results found with the radical clock method.[11] This means that dehydrogenation mediated by titanocene chloride is a radical reaction. With respect to disubstituted epoxy esters **8** and **11**, the mechanism proposed in Scheme 2 (R = H) would operate for deoxygenation and the one proposed in Scheme 6 would operate for deformylation; the reduction in the incipient secondary radical with Ti^{III} is much faster than β-scission of acetate. In the case of epoxy formate **8**, the reduction of the secondary radical with Ti^{III} is only slightly faster than β-scission of formate.

The scope and limitations of the elimination reaction shown above were studied with a new series constituted by *secondary* epoxy alcohol **13** and its ester derivatives, which could react with titanocene chloride through alternative competing pathways. The results are summarized in Table 2.

The reaction of titanocene chloride with epoxy alcohol **13** afforded a mixture with a similar ratio of dehydroxylation **14**, dehydrogenation **2**, and deoxygenation **15** products. This result is quite different from that found for primary epoxy alcohol **1**, and it suggests that the secondary hydroxy group is the worst leaving group. Thus, the rate constant for β-scission of secondary hydroxy groups must be lower than that of primary ones and close to that of β-hydrogen scission.

Table 2. Cp_2TiCl-induced eliminations on epoxy alcohol **13** and its esters.

Entry	Epoxide (R = *n*-hexyl)	Products and Yield
1	**13**	**14** 34% + **2** 27% + **15** 23%
2	**16**	**14** 88%
3	**17**	**14** 66% + **18** 17%
4	**19**	**14** 45% + **20** 50%
5	**21**	**22** 88%

Epoxy formate **16** provided deformylation product **14** as the only product in an identical way to primary isomer **3**. However, secondary acetate **17** and benzoate **19**, although affording decarboxylation and dehydrogenation products such as primary isomers **4** and **6**, did not give similar ratios. Whereas for epoxy acetate **17** deacetoxylation was the predominant reaction, debenzoylation and dehydrogenation were almost equal for epoxy benzoate **19**. This means that the decarboxylation of secondary alcohol esters **17** and **19**, promoted by Ti^{III}, is faster than for the primary ones **4** and **6**. The behavior of epoxy benzyl alcohol **21** with Ti^{III} was different from that of alkyl analogue **13**; only the dehydroxylation product was obtained. The phenyl group appeared to activate the elimination of the hydroxy group.

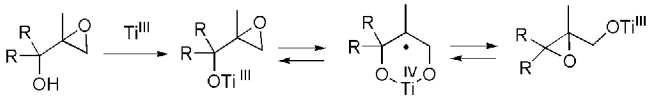
In order to understand the influence of the substitution pattern of the epoxy alcohols on this reaction, we subjected the tertiary epoxy alcohols shown in Table 3 to the reaction with titanocene chloride.

Table 3. Cp_2TiCl-induced eliminations on functionalized epoxides.

Entry	Epoxide	Products and Yield
1	**23** R = *n*-butyl	**24** 27% + **25** 4% + **26** 53%
2	**27**	**28** 43% + **29** 17% + **30** 23%
3	**31**	**32** 39% + **33** 28% + **34** 18%
4	**35**	**32** 28% + **33** 16% + **34** 43%

The reaction of tertiary epoxy alcohol **23** with titanocene afforded expected dehydroxylation product **24** and dehydrogenation product **25**. However, the major product was deoxygenation product **26**. This compound would not arise by oxirane cleavage and further reduction and elimination (see Scheme 2) because the incipient tertiary radical would not be reduced in this way, as has been demonstrated.[9]

The reduction rate was too low. Therefore, we suggest that the deoxygenation process could be explained in terms of an equilibrium between the starting epoxy alcohol and the regioisomer through a six-membered Ti^{IV} intermediate.[14] In this case, the equilibrium was clearly displaced to the right (Scheme 7).



Scheme 7. Equilibration of intermediates.

Phenyl methyl epoxy alcohol **27** gave dehydroxylation product **28** and dehydrogenation product **29**, as expected; unsaturated diol **30** was also obtained. The first and second products would arise through the incipient radical from oxirane cleavage, and further titanocene oxide or titanocene hydride elimination, respectively. The formation of diol **30** would be explained by epoxide isomerization, followed by regioselective oxirane cleavage and dehydrogenation.

Finally, diphenyl epoxy alcohol **31** provided mainly dehydroxylation product **32**, diol **33**, and methyl ketone **34**. The formation of the latter two products could be explained in terms of the interconversion of epoxy alcohol **31** into isomer **35**. To test this interconversion, already proposed in Scheme 7, epoxy alcohol **35** was treated with titanocene chloride. The products obtained from this reaction were exactly the same as from **31**, although in a different ratio. Accordingly, a mechanistic hypothesis can be proposed for the reaction of **31** and **35** with Ti^{III}, depicted in Scheme 8. After the formation of Ti^{III}–alkoxide, as an initial step, the interconversion of **31A** into **35A** would occur through a six-membered Ti^{IV} intermediate (see Scheme 7), followed by regioselective oxirane cleavage to **31B**, and elimination of titanocene epoxide to give **31C**. From **35A**, regioselective oxirane cleavage would afford **35B**, which could evolve, by reduction with Ti^{III}, to give **35C**, or by elimination of CH_2O-Ti^{IV} in a similar manner as the diradical **B** in Scheme 6, to give **35D**.[15] The **31A/35A** equilibrium was displaced to **35A** because the ratio of products **33**+**34** was always higher than **32**.

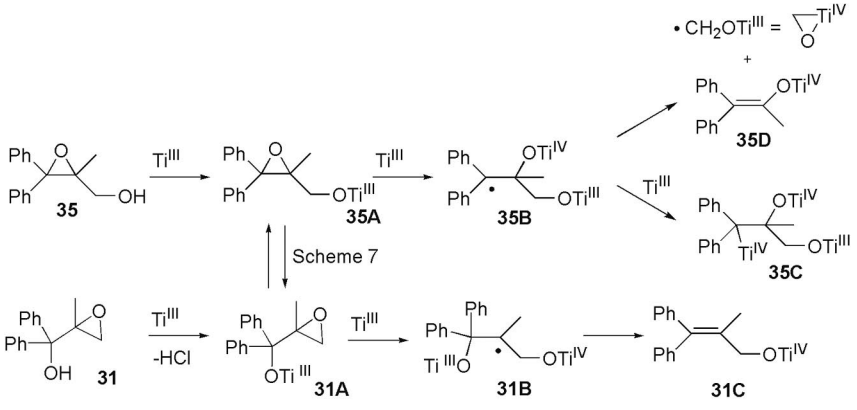
Conclusions

The reaction of a series of 2,3-epoxy alcohols and the corresponding formates, acetates, and benzoates, promoted by Cp_2TiCl has been studied. The different outcome of the reaction of epoxy derivatives has been rationalized in terms of mechanistically biased processes. After homolytic oxirane cleavage, four main types of reaction were found: dehydroxylation, decarboxylation, dehydrogenation, and deoxygenation. The reaction products varied according to the substitution pattern.

The primary alcohol trisubstituted epoxide system and its formate led to hydroxy or formyloxyl elimination. The corresponding epoxy acetate and epoxy benzoate mainly provided the elimination of hydrogen. The disubstituted epoxides mainly afforded the deoxygenation product. The secondary alcohol trisubstituted epoxide system and its esters mainly afforded products from dehydroxylation or decarboxylation. The tertiary alcohol trisubstituted epoxide system afforded deoxygenation as the major product when the *gem* substituents to hydroxy were alkyl groups, and the dehydroxylation product when they were phenyl groups. Another conclusion is that elimination of the hydroxy groups is faster for primary alcohols. Among the esters, the formyloxyl was the fastest leaving group. The acetate and benzoate of the secondary alcohols were eliminated faster than the primary ones. A rare reaction of radical CH_2OTiCp_2Cl elimination has been found.

Experimental Section

General Remarks: Melting points are uncorrected. ^1H NMR spectra were measured at either 200 or 400 MHz and ^{13}C NMR spectra were measured at 50 or 100 MHz in $CDCl_3$ and referenced to sol-



Scheme 8. Proposed mechanism for reaction of epoxy alcohols **31** and **35** with Cp_2TiCl.

vent, except where otherwise indicated. IR spectra were recorded for neat samples on NaCl plates, unless otherwise noted. Standard mass spectrometry data were acquired by using a GC–MS system in EI mode with a maximum *m/z* range of 600. When required, all solvents and reagents were purified by standard techniques: tetrahydrofuran (THF) was purified by distillation from sodium and benzophenone and degassed before use. All reactions were conducted under a positive pressure of argon by using standard benchtop techniques for the handling of air-sensitive materials. Chromatographic separations were carried out under pressure on silica gel using flash column techniques on Merck silica gel 60 (0.040–0.063 mm). Unless otherwise mentioned yields reported are for chromatographically pure isolated products.

General Procedure 1 (GP1): A mixture of Cp_2TiCl_2 (2.20 mmol) and Zn (6.60 equiv.) in strictly deoxygenated THF (10 mL) was stirred at room temperature until the red solution turned green. In a separate flask, the epoxy compound (1 mmol) was dissolved in strictly deoxygenated THF (10 mL). The green Ti^{III} solution was slowly added by cannula to the epoxide solution. After 30 min, an excess amount of saturated NaH_2PO_4 was added, and the mixture was stirred for 20 min. The mixture was filtered to remove insoluble titanium salts. The product was extracted into ether, and the combined organic layer was washed with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and filtered. After removal of the solvent, the crude product was purified by flash chromatography.

Reaction of (3-Hexyl-2-methyloxiran-2-yl)methanol (1) with Cp_2TiCl: According to GP1, reaction of **1** (87 mg, 0.50 mmol) with Cp_2TiCl followed by flash chromatography (hexane/diethyl ether, 8:2) furnished **2** (67 mg, 85%). IR: $\tilde{\nu}$ = 3370, 2957, 2930, 2859, 1653, 1458, 1377, 1262, 1113, 1030 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3 H, 9-H), 1.2–1.6 (m, 10 H), 1.72 (s, 3 H, Me), 4.05 (t, J = 6.5 Hz, 1 H, 3-H), 4.83 (s, 1 H, 1-H), 4.93 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 17.4 (CH_3), 22.5 (CH_3), 25.5 (CH_3), 29.2 (CH_3), 31.7 (CH_3), 34.9 (CH_3), 76.0 (CH_3), 110.8 (CH_3), 147.7 (C) ppm. MS (EI): *m/z* (%) = 156 (3) [M^+], 113 (11), 99 (11), 94 (12), 86 (18), 71 (100), 55 (20). HRMS (ESI): calcd. for $C_{10}H_{20}ONa$ 179.1412; found 179.1401. $C_{10}H_{20}O$ (156.15): calcd. C 76.86, H 12.90; found C 76.98, H 12.94.

Reaction of (3-Hexyl-2-methyloxiran-2-yl)methyl Acetate (4) with Cp_2TiCl: According to GP1, reaction of **4** (103 mg, 0.51 mmol) with Cp_2TiCl followed by flash chromatography (hexane/diethyl ether, 8:2) furnished **2** (22 mg, 25%) and **5** (64 mg, 64%). Data for **5**: IR: $\tilde{\nu}$ = 3436, 2929, 2857, 1742, 1461, 1373, 1238, 1038, 912 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (m, 3 H, 9-H), 1.1–1.6 (m, 10 H), 2.08 (s, 3 H, Me), 4.16 (t, J = 6.5 Hz, 1 H, 3-H), 4.60 (d, J = 13.4 Hz, 1 H, 1-H), 4.66 (d, J = 13.4 Hz, 1 H, 1-H), 5.14 (br. s, 1 H, =CH_2), 5.20 (br. s, 1 H, =CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 20.9 (CH_3), 22.5 (CH_2), 25.6 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 35.5 (CH_2), 63.9 (CH_2), 73.4 (CH), 113.6 (CH_2), 146.2 (C), 170.8 (C) ppm. MS (EI): *m/z* (%) = 196 (1) [M^+ – 18], 154 (1), 129 (50), 113 (6), 97 (21), 87 (95), 69 (55), 55 (100). HRMS (ESI): calcd. for $C_{12}H_{22}O_3Na$ 237.1461; found 237.1461. $C_{12}H_{22}O_3$ (214.16): calcd. C 67.26, H 10.35; found C 67.11, H 10.39.

Reaction of (3-Hexyloxiran-2-yl)methyl Formate (8) with Cp_2TiCl: According to GP1, reaction of **8** (170 mg, 0.91 mmol) with Cp_2TiCl followed by flash chromatography (hexane/diethyl ether, 9:1) furnished **9** (67 mg, 44%) and **10** (40 mg, 30%). Data for **10**: IR: $\tilde{\nu}$ = 3334, 1010 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, J = 6.2 Hz, 3 H, 9-H), 1.21 (m, 10 H), 3.98 (q, J = 6 Hz, 1 H, 3-H), 5.01 (d, J = 10.4 Hz, 1 H, 1-H), 5.14 (d, J = 17.2 Hz, 1 H, 1-H), 5.78 (ddd, J = 6, 10.4, 17.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (CH_3), 22.4 (CH_2), 25.1 (CH_2), 29.0 (CH_2), 31.6 (CH_2), 36.9 (CH_2), 73.0 (CH), 114.1 (CH_2), 141.3 (CH) ppm. HRMS (ESI): calcd. for $C_9H_{18}ONa$ 165.1255; found 165.1259. $C_9H_{18}O$ (142.14): calcd. C 76.00, H 12.76; found C 76.08, H 12.74.

Reaction of 1-(2-Methyloxiran-2-yl)heptan-1-ol (13) with Cp_2TiCl: According to GP1, reaction of **13** (102 mg, 0.58 mmol) with Cp_2TiCl followed by flash chromatography (hexane/diethyl ether, 8:2) furnished **14** (32 mg, 34%), **2** (25 mg, 27%), and (hexane/diethyl ether, 2:8) **15** (23 mg, 23%). Data for **15**: IR: $\tilde{\nu}$ = 3353, 2932, 1449, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, 9-H), 1.2–1.6 (m, 10 H), 4.16 (d, J = 13.2 Hz, 1 H, 1-H), 4.23 (t, J = 6.8 Hz, 1 H, 3-H), 4.30 (d, J = 13.2 Hz, 1 H, 1-H), 5.09 (s, 1 H, =CH_2), 5.12 (s, 1 H, =CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5 (CH_2), 25.6 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 35.7 (CH_2), 64.0 (CH_2), 74.7 (CH), 112.4 (CH_2), 149.9 (C) ppm. HRMS (ESI): calcd. for $C_{10}H_{20}O_2Na$ 195.1356; found 195.1355. $C_{10}H_{20}O_2$ (172.15): calcd. C 69.72, H 11.70; found C 69.67, H 11.68.

Reaction of 5-(2-Methyloxiran-2-yl)nonan-5-ol (23) with Cp_2TiCl: According to GP1, reaction of **23** (150 mg, 0.75 mmol) with Cp_2TiCl followed by flash chromatography (hexane/diethyl ether, 9:1) furnished **26** (77 mg, 53%), **24** (35 mg, 27%), and (hexane/diethyl ether, 1:9) **25** (6 mg, 4%). Data for **24**: IR: $\tilde{\nu}$ = 3357, 2929, 1462, 1134, 1008 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.90 (m, 6 H, 7-H, 4′-H), 1.2–1.4 (m, 8 H), 1.73 (s, 3 H, Me), 2.00 (m, 4 H), 4.10 (s, 2 H, 1-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (2 CH_3), 16.0 (CH_3), 22.8 (CH_2), 29.5 (CH_2), 30.5 (CH_2), 31.6 (CH_2), 31.9 (CH_2), 32.3 (CH_2), 63.7 (CH_2), 127.7 (C), 138.6 (C) ppm. HRMS (ESI): calcd. for $C_{12}H_{24}ONa$ 207.1719; found 207.1728. $C_{12}H_{24}O$ (184.18): calcd. C 78.20, H 13.12; found C 78.38, H 13.16. Data for **25**: IR: $\tilde{\nu}$ = 3364, 2935, 1455, 1128, 999 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (m, 6 H, 7-H, 4′-H), 1.2–1.7 (m, 12 H), 4.15 (s, 2 H, 1-H), 4.98 (s, 1 H, =CH_2), 5.17 (s, 1 H, =CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (2 CH_3), 23.0 (2 CH_2), 25.5 (2 CH_2), 40.7 (2 CH_2), 65.0 (CH_2), 77.5 (C), 111.4 (CH_2), 148.1 (C) ppm. HRMS (ESI): calcd. for $C_{12}H_{24}ONa$ 207.1719; found 207.1726. $C_{12}H_{24}O$ (184.18): calcd. C 78.20, H 13.12; found C 78.08, H 13.15.

Reaction of (2-Methyloxiran-2-yl)diphenylmethanol (31) with Cp_2TiCl: According to GP1, reaction of **31** (103 mg, 0.42 mmol) with Cp_2TiCl followed by flash chromatography (hexane/diethyl ether, 7:3) furnished **34** (16 mg, 18%), **32** (39 mg, 39%), and **33** (28 mg, 28%). Data for **34**: IR: $\tilde{\nu}$ = 2900, 1705, 1451, 1353, 1168 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, 3-H), 5.14 (s, 1 H, 1-H), 7.2–7.4 (m, 10 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.0 (CH_3), 65.0 (CH), 127.2 (2 CH), 128.7 (4 CH), 128.9 (4 CH), 138.2 (2 C), 206.5 (C) ppm. MS (EI): *m/z* (%) = 210 (1) [M^+], 167 (100), 152 (20), 139 (3), 128 (2), 115 (3), 102 (1), 82 (4), 63 (6), 43 (12). HRMS (ESI): calcd. for $C_{15}H_{14}ONa$ 233.0942; found 233.0948. Data for **32**: IR: $\tilde{\nu}$ = 3363, 2910, 1449, 1121 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, Me), 4.18 (s, 2 H, 1-H), 7.1–7.3 (m, 10 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0 (CH_3), 64.9 (CH_2), 126.6 (CH), 126.8 (CH), 127.9 (2 CH), 128.0 (2 CH), 129.5 (2 CH), 129.5 (2 CH), 133.4 (C), 140.5 (C), 141.9 (C), 142.3 (C) ppm. MS (EI): *m/z* (%) = 224 (10) [M^+ – 16], 206 (8), 191 (12), 178 (4), 167 (100), 152 (3), 139 (1), 103 (15), 91 (18), 77 (11), 51 (13). HRMS (ESI): calcd. for $C_{16}H_{16}O_2Na$ 263.1043; found 263.1045. $C_{16}H_{16}O_2$ (240.11): calcd. C 79.97, H 6.71; found C 79.88, H 6.72. Data for **33**: IR: $\tilde{\nu}$ = 3401, 2929, 1462, 1046 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, Me), 3.39 (d, J = 10.0 Hz, 1 H, 1-H), 3.53 (d, J = 10.0 Hz, 1 H, 1-H), 3.98 (s, 1 H, 3-H), 7.2–7.3 (m, 6 H, Ph), 7.5–7.6 (m, 4 H,

Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1 (CH_3), 58.6 (CH), 69.3 (CH_2), 75.0 (C), 126.6 (CH), 126.7 (CH), 128.3 (2 CH), 128.5 (2 CH), 129.6 (2 CH), 129.7 (2 CH), 140.9 (C), 141.2 (C) ppm. MS (EI): *m*/*z* (%) = 211 (3) [M^+ – 31], 168 (100), 152 (8), 133 (6), 115 (5), 105 (18), 91 (11), 75 (63), 57 (58). HRMS (ESI): calcd. for $C_{16}H_{18}O_2Na$ 265.1199; found 265.1207. $C_{16}H_{18}O_2$ (242.13): calcd. C 79.31, H 7.49; found C 79.46, H 7.47.

Supporting Information (see footnote on the first page of this article): Experimental procedures, spectroscopic data, and copies of selected ^1H and ^{13}C NMR spectra.

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