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Chiral Derivatives of Titanium with Terpene Alcohols

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Abstract — A series of substituted alkoxy compounds of titanium were prepared by reactions of titanium isopropylate with 1-menthol, 1-borneol, (±)-isoborneol, and (–)-*trans*-3-hydroxymyrtanol. The specific rotation of the alcoholates was shown to be an additive function of the number of the terpene ligands. For titanium bornylates, the optical activity is a linear function of the degree of substitution. For *trans*-3-hydroxymyrtanol derivatives, an inversion of the optical rotation angle is observed along with an additive dependence of the optical activity on the degree of substitution.
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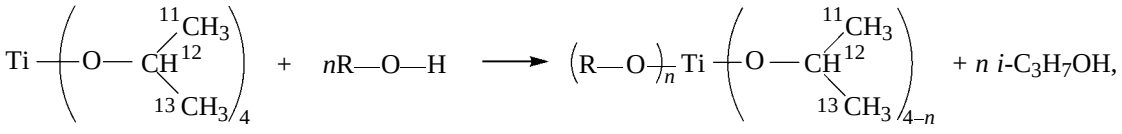
Titanium alkoxy compounds are widely used for preparing high-purity oxides, as cross-linking agents for epoxy and polyester resins, as components of polymeric materials, and as starting compounds for organometallic synthesis. Along with these traditional applications, recently there has been much interest in chiral titanium complexes with optically active ligands. Such complexes are used in organometallic and organic chemistry as reagents and catalysts of various reactions [1–3], e.g., the Diels–Alder reaction [4, 5] (in which both alcoholates and sterically hindered phenolates of titanium are used [6]), enantioselective addition to carbonyl groups [7, 8], polymerization of olefins [3], epoxidation of unsaturated compounds [9, 10], and preparation of optically active titanium-containing monomers and polymers [11].

The most convenient route to alkoxy and aryloxy compounds of titanium is the reaction of the corresponding alcohol with titanium ethylate, isopropylate, or butylate [3, 8, 10–14]. Papers concering titanium compounds with terpene alcohols are relatively few. In particular, Perez et al. [10], among titanium complexes with bulky alkoxyl ligands, described the preparation of mono-, di-, and tetramenthylates. However, no data on their optical activity were given. Klabunovskii et al. [11] reported on the synthesis of a series of titanium-containing monomers by stepwise interchange of titanium ethylate and butylate with optically active alcohols. Among other products, they prepared and described a mixed monomer $Ti(OR^1)_2(OR^2)(OR^3)$, where R^1 = *n*-Bu, R^2 = $CH_2CH_2OCOC(CH_3)=CH_2$, and R^3 = Ment. The optical activity of the compounds prepared was measured at various wavelengths, and abnormally high values were obtained for the menthylates. The monomers obtained were used for the subsequent preparation of titanium-containing polymers. Davis et al. [3] described the preparation of mixed derivatives of titanium with binaphthol and menthol or borneol [$Ti(OR^1)(OR^2)_2$, where R^1 = BIN, R^2 = Ment, Born], with the aim of subsequent separation of binaphthol stereoisomers. In this case, binaphthol coordinates to titanium in the bidentate fashion [3, 8, 12]. Titanium derivatives with such bidentate ligands as bisphenols [13] and butanediol [14] have been reported. In most cases, titanium menthylates and bornylates were used as intermediates or catalysts. The optical properties of the terpene alcoholates proper either were not considered at all [3, 10], or ambiguous data were obtained [11].

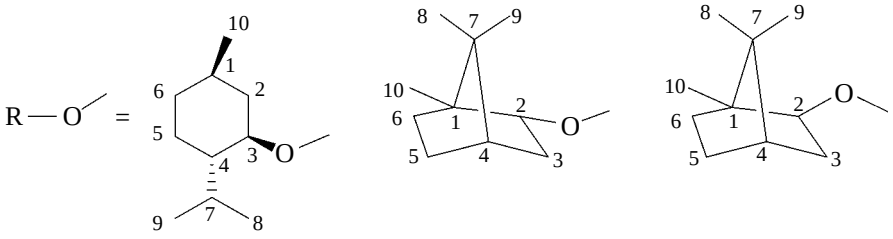
The goal of this study was to prepare terpene alcoholates of titanium with optically active *l*-menthol **I**, *l*-borneol **II**, (±)-isoborneol **III**, and (–)-*trans*-3-hydroxymyrtanol **IV** and to examine their optical properties. The compounds were prepared by the reactions of titanium isopropylate with the terpene alcohols.

The reactants were taken in strictly stoichiometric amounts. To shift the equilibrium toward formation of alcoholates, the released isopropanol was distilled off in the course of the synthesis together with a part of the solvent. To prepare compounds **VI**–**VIII**, solutions of the alcohols and diol were added into a solution of titanium isopropylate. In the synthesis of **XIX**, the order was inverse. With monohydric alcohols (menthol, borneols), both mixed and fully substituted alcoholates are obtained. We expected that primary hydroxy groups of diol **IV** (at C^{10}) would react faster

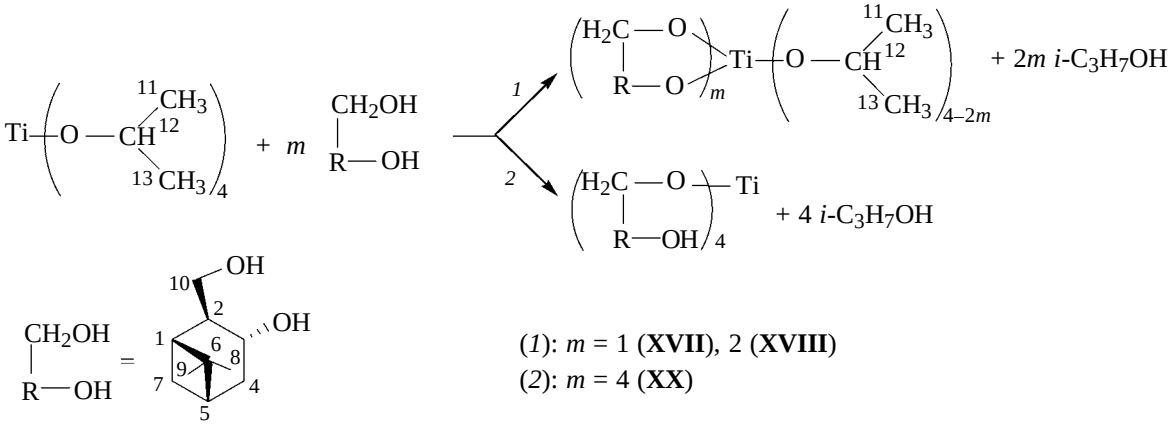


V **I–III** **VI–XVI**

n = 1 (**VI, X, XIV**), 2 (**VII, XI, XVI**), 3 (**VIII, XII, XVI**), 4 (**IX, XIII**).



I, VI–IX **II, X–XIII** **III, XIV–XVI**



(*1*): *m* = 1 (**XVII**), 2 (**XVIII**)
(*2*): *m* = 4 (**XX**)

than secondary groups (at C^3) and, correspondingly, addition of the alcohol to titanium isopropylate would yield compounds **XVII** and **XVIII** with the bidentate alkoxy groups, whereas addition of titanium isopropylate to the alcohol would yield compound **XIX** with the monodentate alkoxy groups. This is indeed the case, as judged from the amounts of the released isopropanol, spectroscopic data, and optical activity of **XVII**–**XIX**.

Menthol and borneol completely replace all the four isopropyl groups. In the reaction with isoborneol, replacement of the four isopropyl ligands was incomplete, which is caused by steric hindrance (computer simulation indicates that coordination of four isobornyl groups is impossible). All the products obtained are individual compounds. Titanium alcoholates are readily soluble in dry hydrocarbons and more resistant to hydrolysis than the related aluminum compounds [15, 16].

IR AND NMR SPECTRA

Mentylates VI–IX. The IR and ^{1}H NMR spectra of the compounds prepared are similar to those described in [10, 11]. The ^{1}H NMR spectra of all the four menthylates suggest that the terpene ligands in them are coordinated with the titanium atom. In the spectra of **VI** and **VII**, the signals of both OCH and methyl groups of the terpene and isopropyl fragments are clearly resolved. The observed intensity ratios of the signals from the methyl groups of the terpene and isopropyl fragments (1 : 1 for **VI** and 1 : 2 for **VII**) are consistent with the suggested structures.

Bornylates X–XIII. In the ^{1}H NMR spectra of mixed bornylates **X**–**XII**, there are two pais of OCH signals related to bornyl and isopropyl groups. As compared to the corresponding signals in the spectrum of borneol **II**, their splitting pattern in the spectra of **X**–**XIII** is different. As the isopropyl groups are replaced, the intensity of their methyl signals regularly decreases. Broadening of the methyl signals of the bornyl groups and changes in their splitting pattern in the spectra of **X**–**XIII**, compared to **II**, are indicative of the coordination of bornyl groups to the Ti atom. The position of signals in the spectra of **X**–**XIII** is close to that reported for bornyl derivatives in [3].

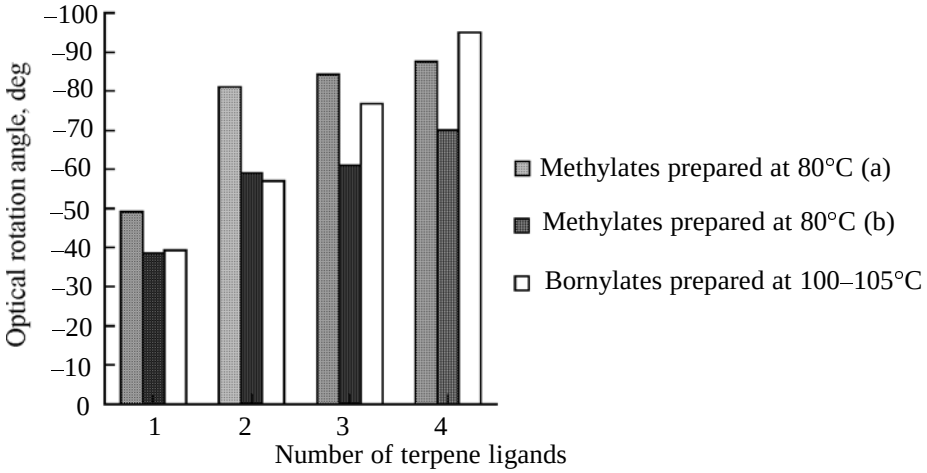


Fig. 1. Optical activity of titanium *l*-menthylates **VI**–**IX** and *l*-bornylates **X**–**XIII**.

Isobornylates XIV–XVI. In the ^{1}H NMR spectra, the OCH signals of the isopropyl and isobornyl residues largely overlap, and the coordination mode can be judged from the intensities of the corresponding methyl signals. With an increase in the number of terpene groups, the intensity ratio of the methyl signals (isopropyl : isobornyl) decreases. This ratio is 3 : 1 for **XIV** and 2 : 3 for **XV**. Compound **XVI** gives no signals assignable to isopropyl groups. In going from alcohol **III** to alcoholates **XV** and **XVI**, the methyl groups become nonequivalent, and the C^9 signal is shifted from ~0.90 to ~1.25 ppm.

In the spectra of **VI**–**XVI**, the splitting pattern of some signals observed in the range characteristic of isopropyl OCH groups (~4.40 – 4.80 ppm, septet expected) was unclear, apparently because of insufficient resolution of the spectrometer. Therefore, the signals in this range are given as multiplets.

Hydroxymyrtanol derivatives XVII–XIX. The ^{1}H and ^{13}C NMR spectra of these compounds are poorly informative. The signals of the OH groups at C^{10} and C^3 in the spectrum of diol **IV** (the related signals in the spectra of the other alcohols are strong) are weak and overlap with the C^2H and $C^{10}H_2O$ signals. The $C^{10}H_2O$ and OC^3H signals in the ^{1}H NMR spectra of alcoholates **XVII**–**XIX**, compared to diol **IV**, are also multiplet, but are split into a larger number of lines. In the spectrum of **XVIII**, there is a weak, and in the spectrum of **XIX**, a strong multiplet of the hydroxyl hydrogen at C^3 at ~3.7 ppm. The ^{13}C NMR spectra of **XVII**–**XIX** are characterized by only slight (3–4 ppm) shifts of the C^{10} and C^3 signals relative to diol **IV**.

The IR spectra of **XVIII** and **XIX** contain bands of hydroxy groups. In the spectrum of **XVIII**, these bands are weak, and in that of **XIX**, strong. This fact, in combination with the NMR data, suggests different coordination modes of the ligands (both mono- and bidentate) in **XVIII**. Taking also into account data on the optical activity of the compounds, we can suggest the presence of mostly bidentate ligands (bound via oxygen at C^{10} and C^3) in **XVII** amd **XVIII** and of monodentate ligands (bound via oxygen at C^{10}) in **XIX**.

OPTICAL ACTIVITY OF ALCOHOLATES

The specific rotation angles of titanium menthylates and bornylates are plotted in Fig. 1. In contrast to aluminum *l*-menthylates and *l*-bornylates (whose optical activity is close to that of the free alcohols, menthol **I** and borneol **II** [15, 16]), the optical activity of the titanium derivatives is an additive quantity with respect to the activity of separate groups. The rotation angle of bornylates **X**–**XIII** is a virtually linear function of the number of optically active groups.

The rotation angle of menthylates **VI** and **VII** increases by a factor of approximately 2 on coordination of the first two groups. Coodination of the third and fourth groups in **VIII** and **IX** leads to only a slight increase in the rotation angle. We also found that the optical activity of samples **VIa**–**IXa** prepared in refluxing benzene is systematically higher than that of samples **VIb**–**IXb** prepared in refluxing toluene. The trends of variation of the rotation angle are similar in both groups. This pattern differs from that observed with aluminum menthylates [15, 16] in which the optical activity was essentially independent of the number of coordinated menthyl groups. In the case of titanium derivatives, the observed trend might be

attributed to racemization (isomerization) of menthyl residues above 100°C. To check this assumption, we hydrolyzed samples of alcoholates **VIb**, **VIIb**, and **IXb** prepared in refluxing toluene. The specific rotation angles of the isolated samples of *l*-menthol were –47.7°, –44.6°, and –43.7°, respectively (for the starting menthol **I**, $[\alpha]_D^{20}$ –46.0°). Thus, heating to 100–110°C does not cause noticeable racemization of the menthyl residues.

Apparently, this character of the optical activity of menthylates **VI**–**IX** is associated with the features of coordination of the menthyl ligands to the titanium atom. In **VI** and **VII**, both groups are arranged freely. At high degrees of substitution in **VIII** and **IX**, the arising steric hindrance may lead to changes in the coordination pattern. Increasing temperature can lead to similar structural disordering.

In hydroxymyrtanol derivatives **XVII**–**XIX**, inversion of the rotation angle was observed along with the additive trend (Fig. 2). Whereas the starting diol **IV** is levorotatory, all its titanium derivatives **XVII**–**XIX** are dextrorotatory. Coordination of one and two ligands in **XVI** and **XVII** leads virtually to doubling of the rotation angle (+18.8° and +34.3°, respectively), which may be due to the presence of one and two bidentate groups. Coordination of four ligands in **XIX** increases the angle to +38.5°, suggesting the presence of monodentate ligands in **XIX**. The same conclusion follows from calculations of the possible molecular geometries of **XVII**–**XIX**.

EXPERIMENTAL

The metal content of the samples was determined by combustion. Gas-chromatographic analyses were performed on a Chrom-5 chromatograph (3000 × 3.0-mm column, carrier gas He, sorbent SKTF rubber). Thin-layer chromatography was performed on Silufol plates, which were developed with a 3% solution of vanillin in ethanol. The melting points were determined with a TP melting device. The optical rotation angles were measured with a Polatronic MHZ polarimeter using solutions of substances in benzene (2.0–20.0 g/100 ml). The IR spectra were recorded from KBr pellets with an MIR-80 spectrometer in the range 4000–400 cm^{-1}. The ^1H and ^{13}C NMR spectra were taken on Tesla BS-497A (80 MHz) and Bruker (300 MHz) devices in C_6D_6 and $CDCl_3$. The molecular geometries were simulated using appropriate software.

Starting Chemicals

***l*-Menthol (I),** mp 41–42°C. $[\alpha]_D^{20}$ –46.0° (*C* 10.0 g per 100 ml, ethanol), pure grade. Purified by vacuum distillation (130°C/1 mm Hg). Snow-white crystals.

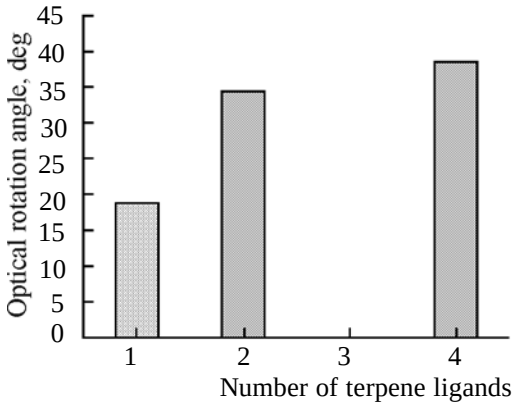


Fig. 2. Optical activity of titanium derivatives with hydroxymyrtanol **XVII**–**XIX**.

***l*-Borneol (II),** mp 201–202°C. $[\alpha]_D^{20}$ –36.0° (*C* 10.0 g/100 ml, ethanol), pure grade.

(±)-Isoborneol (III), mp 208–210°C, pure grade.

Both borneols were purified by sublimation (100°C/1 mm Hg). Colorless waxy substances.

Titanium isopropylate (V), chemically pure grade, produced by electrolysis. Colorless liquid, main substance content ≥99.5%. Used without additional purification.

(–)-*trans*-*s*-Hydroxymyrtanol (IV) [17]. A solution of 3.3 g of conc. H_2SO_4 in 10 ml of ether was added dropwise to a solution of 5 g of myrtenol ($[\alpha]_D^{20}$ +20.4°) and 1.45 g of $LiBH_4$ in 60 ml of absolute ether. The mixture was stirred under nitrogen at room temperature. The alcohol disappeared within 2 h (TLC monitoring). Then 5 ml of water, 7 ml of 10% NaOH, and 7 ml of 30% H_2O_2 were added, and the mixture was stirred for an additional 1 h. The reaction products were extracted with ether, and the extract was washed with a NaCl solution and dried over anhydrous $MgSO_4$. The desired product, *trans*-3-hydroxymyrtanol, was isolated by crystallization from hexane–ether; yield 4.45 g (79%), mp 65–72°C, $[\alpha]_D^{20}$ –16.2° (*C* 2.9 g/100 ml, ethanol).

IR spectrum, ν, cm^{-1}: 3316, 3000, 2936, 1652, 1632, 1472, 1450, 1388, 1370, 1330, 1300, 1260, 1216, 1152, 1104, 1086, 1036, 1016, 988, 970, 954, 928, 900, 872, 856, 832, 824, 672, 528, 460. ^1H NMR spectrum (300 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.80 s (3H, C^9H_3), 1.08 d (1H, C^7H_2-*exo*, *J* 9,7), 1.18 s (3H, C^8H_3), 1.74 d.d.d (1H, C^7H_2-*endo*, J_1 12, J_2 1.5, J_3 1.5), 1.86 m (2H, C^4H_2-*endo*, *exo*), 2.04 m (1H, C^1H), 2.39–2.54 m (2H, C^2H, $C^{10}OH$), 3.40–3.56 m (1H, C^3OH), 3.56–3.75 m (2H, $C^{10}H_2$), 4.25–4.32 m

(1H, C^3H). ^{13}C NMR spectrum (75 MHz, C_6D_6), δ_C, ppm: 23.9 C^9, 27.3 C^8, 33.6 C^7, 37.7 C^4, 37.9 C^6, 41.6 C^5, 43.2 C^2, 55.3 C^1, 66.3 C^{10}, 67.5 C^3.

Preparation and Characteristics of Compounds

Menthylates and bornylates. All the syntheses were performed in a three-necked round-bottomed flask equipped with a stirrer and a reflux condenser, in refluxing absolute benzene or toluene under argon. Weighed portions of *l*-menthol, *l*-borneol, or isoborneol (0.01, 0.02, 0.03, or 0.042 mol depending on the desired ratio) were dissolved in 20 ml of the solvent, and the solutions were added dropwise with continuous stirring over a period of 6–8 h to a solution of 0.01 mol ot titanium isopropylate in 50 ml of the same solvent. In the course of the synthesis, up to 20–25 ml of the solvent was distilled off and then analyzed for the isopropanol content. After adding the whole amount of the isopropylate, the mixture was stirred for an additional 2–4 h and allowed to fully settle, after which the solvent was completely removed on a rotary evaporator. In the synthesis of the tetrasubstituted derivatives, excess alcohols were sublimed off from the residues (90–100°C/1 mm Hg).

Hydrolysis of menthylates. A weighed portion of the product (60–100 mg) was placed in a 10-ml flask, 2 ml of 10% HCl was added, and the mixture was stirred until it became turbid, after which it was left for 3 h. Then the acid was neutralized with 5% $NaHCO_3$ to pH 8; in so doing, the mixture became strongly turbid. The organic phase was extracted with 2 ml of toluene and left to completely settle for 2–3 h. The organic layer was transferred into a test tube and kept until the phase separation was complete. The aqueous phase was returned to the flask used for the hydrolysis. The liquid in the test tube was diluted with toluene to 2.0 ml and taken for optical measurements. To evaluate the completeness of menthol recovery, repeated extraction with 1.0 ml of toluene was performed as described above. Both extracts were analyzed by GLC for the menthol content; its recovery was almost quantitative even in the first extraction.

Menthylates VI–IX were prepared as crystallizing oils with various tints of yellow color (from light yellow for **V** to straw-yellow for **IX**).

Monosubstituted derivative Ti(i-PrO)$_3$(MentO). *Sample **VIa***. Reaction for 5 h in refluxing benzene. Yield 77.5%. Found Ti, %: 13.2. Calculated Ti, %: 12.64. $[\alpha]_D^{20}$ –49.0° (*C* 6.0 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2968, 2928, 2876, 2632, 1460, 1368–1380, 1364, 1128, 1084, 1068, 1052, 1008, 932, 856, 732, 694, 624. ^1H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.97 s (3H, $C^{10}H_3$), 1.04 s (3H, $C^{8,9}H_3$), 1.13 s (3H, $C^{8,9}H_3$), 1.34 d (18H, $6C^{11,13}H_3$, *J* 6.5), 1.42–3.00 m (9H, $3C^{2,5,6}H_2$, $3C^{1,4,7}H$), 3.90–4.30 m (3H, OC^3H), 4.50–4.80 m (1H, $OC^{12}H$).

*Sample **VIb***. Reaction for 8.5 h in refluxing toluene. Yield 90.5%. Found Ti, %: 12.6. Calculated Ti, %: 12.64. $[\alpha]_D^{20}$ –38.5° (*C* 15.5 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2968, 2928, 2876, 2632, 1460, 1380–1368, 1364, 1128, 1084, 1068, 1052, 1008, 932, 856, 732, 694, 624. ^1H NMR spectrum (80 MHz, C_6D_6) δ, ppm (*J*, Hz): 0.99 s (3H, $C^{10}H_3$), 1.05 s (3H, $C^{8,9}H_3$), 1.09 s (3H, $C^{8,9}H_3$), 1.41 d (18H, $6C^{11,13}H_3$, *J* 6.5), 1.60–3.00 m (9H, $3C^{2,5,6}H_2$, $3C^{1,4,7}H$), 3.98–4.30 m (3H, OC^3H), 4.50–4.80 m (1H, $OC^{12}H$).

Disubstituted derivative Ti(i-PrO)$_2$(MentO)$_2$. *Sample **VIIa***. Reaction for 5 h in refluxing benzene. Yield 92.0%. Found Ti, %: 10.2. Calculated Ti, %: 10.05. $[\alpha]_D^{20}$ –81.0° (*C* 4.7 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2964, 2936, 2728, 2632, 1460, 1372–1380, 1336, 1346, 1108, 1084, 1068, 1052, 1000, 930, 856, 726. ^1H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.92 s (6H, $2C^{10}H_3$), 0.99 s (6H, $2C^{8,9}H_3$), 1.09 s (6H, $2C^{8,9}H_3$), 1.31 d (12H, $4C^{11,13}H_3$, *J* 6.5), 1.50–3.00 m (18H, $6C^{2,5,6}H_2$, $6C^{1,4,7}H$), 3.80–4.20 m (2H, $2OC^3H$), 4.40–4.80 m (2H, $2OC^{12}H$).

*Sample **VIIb***. Reaction for 7.5 h in refluxing toluene. Yield 99.0%. Found Ti, %: 9.90. Calculated Ti, %: 10.05. $[\alpha]_D^{20}$ –59.0° (*C* 23.2 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2964, 2936, 2728, 2632, 1460, 1380–1372, 1346, 1336, 1108, 1084, 1068, 1052, 1000, 930, 856, 726. ^1H NMR spectrum (80 MHz, $_C6D6$), δ, ppm (*J*, Hz): 0.96 s (6H, $2C^{10}H_3$), 1.05 s (6H, $2C^{8,9}H_3$), 1.13 s (6H, $2C^{8,9}H_3$), 1.34 d (12H, $4C^{11,13}H_3$, *J* 6), 1.45–3.00 m (18H, $6C^{2,5,6}H_2$, $6C^{1,4,7}H$), 3.90–4.35 m (2H, $2OC^3H$), 4.45–4.80 m (2H, $2OC^{12}H$).

Trisubstituted derivative Ti(i-PrO)(MentO)$_3$. *Sample **VIIIa***. Reaction for 5.5 h in refluxing benzene. Yield 99.0%. Found Ti, %: 8.3. Calculated Ti, %: 8.36. $[\alpha]_D^{20}$ –84.3° (*C* 9.0 g/100 ml, benzene).

*Sample **VIIIb***. Reaction for 8 h in refluxing toluene. Yield 73.7%. Found Ti, %: 8.0. Calculated Ti, %: 8.36. $[\alpha]_D^{20}$ –61.0° (*C* 3.9 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2964, 2936, 2876, 1460, 1388–1372, 1108, 1084, 1068, 1052, 1000, 930, 856, 794, 772, 724. ^1H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 1.14 s (9H, $3C^{10}H_3$), 1.18 s (9H, $3C^{8,9}H_3$),

1.20 s (9H, $3C^{8,9}H_3$), 1.51 d (6H, $2C^{11,13}H_3$, *J* 6), 1.60–3.80 m (27H, $9C^{2,5,6}H_2$, $9C^{1,4,7}H$), 4.05–4.45 m (4H, $3OC^{13}H$, $OC^{12}H$).

Tetrasubstituted derivative Ti(MentO)$_4$. *Sample* ***IXa***. Reaction for 5 h in refluxing benzene. Yield 99.0%. Found Ti, %: 6.9. Calculated Ti, %: 7.16. $[\alpha]_D^{20}$ –87.3° (*C* 8.0 g/100 ml, benzene).

Sample ***IXb***. Reaction for 7.5 h in refluxing toluene. Yield 99.0%. Found Ti, %: 6.90. Calculated Ti, %: 7.16. $[\alpha]_D^{20}$ –70.0° (*C* 19.2 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2928, 2876, 1460, 1372–1388 d, 1348, 1108, 1082, 1068, 1050, 998, 930, 856, 794, 772, 726, 678. ^{1}H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 1.02 s (12H, $4C^{10}H_3$), 1.07 s (12H, $4C^{8,9}H_3$), 1.14 s (12H, $4C^{8,9}H_3$), 1.30–3.90 m (36H, $12C^{2,5,6}H_2$, $12C^{1,4,7}H$), 4.16 t (4H, $4OC^{13}H$, *J* 9).

Bornylates X–XIII were prepared by refluxing the reactants in toluene for 6 h.

Monosubstituted derivative Ti(i-PrO)$_3$(BornO). *Sample* ***X***. Yield 82.0%. Found Ti, %: 12.72. Calculated Ti, %: 12.67. Bright yellow viscous oil. $[\alpha]_D^{20}$ –39.3° (*C* 1.3 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 1462, 1390, 1380, 1360, 1300, 1230, 1202, 1170, 1142, 1114, 1086, 1070, 1042, 1022, 990, 980, 940, 924, 902, 860, 792–780, 702, 672, 648. ^{1}H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.74 s (3H, $C^{10}H_3$), 0.79 s (6H, $2C^{8,9}H_3$), 0.90–2.13 m (7H, $3C^{3,5,6}H_2$, C^3H, 18H; $6C^{11,13}H_3$), 4.65 m (1H, $OC^{12}H$), 4.90–5.00 m (3H, $3OC^{12}H$).

Disubstituted derivative Ti(i-PrO)$_2$(BornO)$_2$. *Sample* ***XI***. Yield 94.5%. Found Ti, %: 10.07. Calculated Ti, %: 10.14. Bright yellow crystallizing oil. $[\alpha]_D^{20}$ –57.0° (*C* 3.3 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 1460, 1392, 1380, 1362, 1300, 1232, 1205, 1172, 1140, 1112, 1085, 1072, 1040, 1023, 992, 982, 942, 920, 900, 860, 790–780, 700, 670, 648. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.84 s (12H, $4C^{10}H_3$), 0.88 s (6H, $2C^{8,9}H_3$), 1.02–1.43 m (8H, $4C^{5,6}H_2$), 1.22 d (12H, $4C^{11,13}H_3$, *J* 7), 1.50–1.80 d (2H, C^4H), 2.00–2.38 m (4H, $2C^{13}H_2$), 4.51 t (2H, $2OC^2H$, *J* 6), 4.65 d (2H, $2OC^{12}H$, *J* 8). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 13.69 C^8, 18.78 C^9, 20.38 C^{10}, 26.39 C^7, 26.63 $C^{11,13}$, 28.38 C^1, 40.49 C^5, 45.28 C^5, 47.58 C^4, 50.90 C^3, 76.18 C^{12}, 90.39 C^2.

Trisubstituted derivative Ti(i-PrO)(BornO)$_3$. *Sample* ***XII***. Yield 77.7%. Found Ti, %: 8.24. Calculated Ti, %: 8.45. Yellow waxy substance. $[\alpha]_D^{20}$ –76.5° (*C* 2.5 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 1460, 1390, 1375, 1360, 1300, 1230, 1200, 1170, 1140, 1110, 1086, 1070, 1040, 1020, 990, 980, 940, 920, 890, 850, 790–780, 700, 675, 650. ^{1}H NMR spectrum (80 MHz, C_6D_6) δ, ppm (*J*, Hz): 0.73 s (9H, $3C^{10}H_3$), 0.78 s (18H, $6C^{8,9}H_3$), 0.81 d (6H, $2C^{11,13}H_3$, *J* 6), 0.83–2.11 m (21H, $9C^{3,5,6}H_2$, $3C^4H$), 4.50–4.90 m (3H, $3OC^2H$), 5.00 m (1H, $OC^{12}H$).

Tetrasubstituted derivative Ti(O-Born)$_4$. Sample ***XIII***. Yield 95.5%. Found Ti, %: 7.9. Calculated Ti, %: 7.26. Straw-colored waxy substance. $[\alpha]_D^{20}$ –95.0° (*C* 11.8 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 1456 d, 1389, 1375, 1358, 1304, 1233, 1204, 1165, 1140, 1111, 1084, 1069, 1036, 1022, 993, 978, 936, 920, 889, 851, 777–793, 702, 673, 652. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.84 s (12H, $4C^{10}H_3$), 0.92 s (24H, $2C^{8,9}H_3$), 1.00–1.32 m (16H, $4C^{5,6}H_2$), 1.58–1.80 m (4H, C^4H), 2.05–2.35 m (8H, $4C^3H_2$), 4.66 d (4H, OC^2H, *J* 9). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 13.64 C^8, 18.72 C^9, 20.34 C^{10}, 24.41 C^7, 28.30 C^1, 40.14 C^6, 45.23 C^5, 47.97 C^4, 50.81 C^3, 90.17 C^2.

Isobornylates XIV–XVI were prepared by refluxing the reactants in toluene for 8 h.

Monosubstituted derivative Ti(*i*-PrO)$_3$(*i*-BornO). *Sample* ***XIV***. Yield 99.2%. Found Ti, %: 12.1. Calculated Ti, %: 12.67. Pale straw-colored viscous oil. IR spectrum, ν, cm^{-1}: 1460, 1380, 1190, 1160, 1115, 1020, 970, 912, 880, 790, 740, 685, 650, 615. ^{1}H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.82 s (3H, $C^{10}H_3$), 1.10 s (3H, $C^{8,9}H_3$), 1.29 d (21H, C^9H_3, $6C^{11,13}H_3$, *J* 6), 1.50–3.00 m (7H, $3C^{3,5,6}H_2$, C^4H), 4.30–4.80 m (4H, OC^2H, 3 $OC^{12}H$).

Disubstituted derivative Ti(*i*-PrO)$_2$(*i*-BornO)$_2$. *Sample* ***XV***. Yield 98.2%. Found Ti, %: 9.7. Calculated Ti, %: 10.14. Viscous straw-colored crystallizing oil. IR spectrum, ν, cm^{-1}: 1460, 1380, 1300, 1190, 1170, 1116, 1022, 970, 910, 880, 790, 745, 690, 652, 610. ^{1}H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.84 s (6H, $2C^{10}H_3$), 1.15 s (6H, $3C^{8,9}H_3$), 1.26 s (6H, $2C^9H_3$), 1.29 d (18H, $2C^9H_3$, $4C^{11,13}H_3$, *J* 5), 1.40–2.70 m (14H, $6C^{3,5,6}H_2$, $2C^{2,4}H$), 4.35–4.75 m (4H, $2OC^2H$, $2OC^{12}H$).

Trisubstituted derivative Ti(*i*-PrO)(*i*-BornO)$_3$. *Sample* ***XVI***. Yield 93.5%. Found Ti, %: 8.6. Calculated Ti, %: 8.45. Pale straw-colored waxy substance. IR spectrum, ν, cm^{-1}: 1456, 1377, 1306, 1244, 1188, 1165, 1134, 1113, 1019, 970, 909, 878, 791, 743, 685, 648, 613. ^{1}H NMR spectrum (80 MHz, C_6D_6), δ, ppm (*J*, Hz): 0.86 s (9H, $3C^{10}H_3$), 1.17 s (9H, $3C^{8,9}H_3$), 1.29 s (9H, $3C^9H_3$), 1.34–2.80 m (27H,

$9C^{3,5,6}H_2$, $3C^{2,4}H$, $2C^{11,13}H_3$), 4.30–4.80 m (4H, $3OC^2H$, $1OC^{12}H$).

***trans*-3-Hydroxymyrtanol derivatives XVII–XIX.** In the synthesis of **XVII** and **XVIII**, we added the alcohol to titanium isopropylate, and in the synthesis of **XIX**, titanium isopropylate to the alcohol. The products are yellow powders readily soluble in benzene and toluene.

Monosubstituted derivative XVII. A solution of 0.644 g of 3-hydroxymyrtanol in 20 ml of toluene was added dropwise over a period of 4 h to a weakly refluxing solution of 1.09 g of titanium isopropylate in toluene, after which the mixture was refluxed for an additional 2 h. The solvent was removed on a rotary evaporator, and the residue was finally dried in a vacuum (80–90°C/1 mm Hg). Yield 1.04 g (87%). Found Ti, %: 14.3. Calculated Ti, %: 14.35. $[\alpha]_D^{20}$ +18.8° (*C* 1.68 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 2932, 1726, 1634, 1470, 1390–1370, 1286, 1148, 1130, 1086, 1034, 990, 954–935, 878, 850, 700, 560. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.88 s (3H, C^9H_3), 1.05 d (1H, C^7H_2-exo, *J* 10), 1.11 s (6H, $C^{11,13}H_3$), 1.20 d (3H, C^8H_3), 1.25 s (6H, $C^{1,3}H_3$), 1.74–1.79 m (1H, C^7H-*endo*), 1.89 d (2H, C^4H_2-*endo*, *exo*), 1.97 s (2H, C^4H_2-*endo*, *exo*), 2.16 m (1H, C^1H), 2.44–2.51 m (1H, C^1H), 3.66–3.76 m (2H, $C^{10}H_2$), 4.35 m (3H, C^3H, $OC^{12}H$). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 22.64 $C^{11,13}$, 23.91 C^9, 27.43 C^8, 34.19 C^7, 37.57 C^4, 37.98 C^6, 41.78 C^5, 43.27 C^2, 55.29 C^1, 58.34 C^{12}, 67.10 C^{10}, 68.32 C^3.

Disubstituted compound XVIII was prepared from 0.579 g of titanium isopropylate and 0.692 g of 3-hydroxymyrtanol in 50 ml of toluene. Synthesis time 9 h. Yield 0.806 g (97%). Found Ti, %: 12.1. Calculated Ti, %: 12.48. $[\alpha]_D^{20}$ +34.3° (*C* 1.1 g/100 ml, benzene). IR spectrum, ν, cm^{-1}: 3444, 2996, 2928, 1637, 1472, 1388, 1370, 1288, 1220, 1150, 1128, 1086, 1050, 990, 944, 878, 852, 786, 708, 632, 562. ^1H NMR spectrum (300 MHz, $CDCl_3$) δ, ppm (*J*, Hz): 0.88 s (3H, C^8H_3), 1.05–1.14 d (1H, C^7H_2-*exo*, *J* 10), 1.20–1.25 d (3H, C^8H_3), 1.74–1.79 m (1H, C^7H_2-*endo*), 1.88 d (2H, C^4H_2-*endo*, *exo*), 1.96 s (2H, C^4H_2-*endo*, *exo*), 2.15 m (1H, C^1H), 2.35–2.46 m (1H, C^2H), 3.65–3.72 m (H, C^3OH), 4.34 m (1H, C^3H). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 23.91 C^9, 27.43 C^8, 34.17 C^7, 37.53 C^4, 37.98 C^4, 38.76 C^4, 41.77 C^5, 43.30 C^2, 55.28 C^1, 67.02 C^{10}, 68.21 C^3.

Tetrasubstituted derivative XIX. A toluene solution of 0.300 g of titanium isopropylate was added dropwise over a period of 6 h to a solution of 0.681 g of 3-hydroxymyrtanol. Yield 0.714 g (98%). Found Ti, %: 8.0. Calculated Ti, %: 7.62. $[\alpha]_D^{20}$ +38.5° (*C* 3.0 g per 100 ml, benzene). IR spectrum, ν, cm^{-1}: 3448 br.s, 2996, 2932, 1638, 1474, 1388, 1372, 1288, 1216, 1148, 1128, 1086, 1036, 988, 944, 878, 854, 812, 775, 700, 625, 560. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.87 s (3H, C^9H_3), 1.07 d (1H, C^7H_2-*exo*, *J* 10), 1.14 s (1H, C^7H_2-*exo*), 1.20–1.25 d (3H, C^8H_3), 1.70–1.80 m (1H, C^7H_2-*endo*), 1.90 d (2H, C^4H_2-*endo*, *exo*), 2.40–2.50 m (1H, C^2H), 3.60–3.80 m (1H, C^3OH), 4.35 m (1H, C^3H). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 23.87 C^9, 27.41 C^8, 34.03 C^7, 37.70 C^4, 37.96 C^6, 41.82 C^5, 43.38 C^2, 55.41 C^1, 66.94 C^{10}, 68.08 C^3.

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