Insertion Reaction of Aldehydes into Zirconacyclopentanes†

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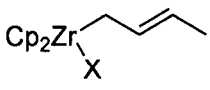
Aldehydes reacted with zirconacyclopentane derivatives *via* insertion into the Zr-sp^3C bond to afford the corresponding 7-membered zirconacycles.

Keywords Aldehyde, ethylene gas, insertion, oxazirconacyle, zirconacyclopentane

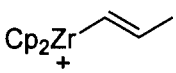
Introduction

Development of new carbon-carbon bond formation reactions using transition metal compounds has attracted much attention. It is of great practical interest to study on the application of readily available organic substrates such as aldehydes in carbon-carbon bond formation reactions. In recent years, zirconocene compounds have been proved to be very useful for organic transformation reactions.[1,2] In principle, two types of reactions of zirconocene compounds with aldehydes have been reported. One involves allylic zirconocene species such as **1**. Crotylzirconium derivatives undergo a rapid reaction with aldehydes affording a useful method for the threo selective synthesis of β-methylhomoallyl alcohols.[3a] Zirconocene enolates were also reported to undergo a facile aldol condensation with aldehydes to give predominantly the erythro products.[3b] Zirconocene-η^4-1, 3-pentadiene complexes, for example, a 2, 4-hexadiene-zirconocene complex, reacted with aliphatic aldehydes, in which double insertion of electrophiles predominated even under mild reaction conditions.[4] The actual reacting species in this reaction was proposed to be the allylic system.[4] The other type involves cationic zirconocene species such as **2**.[5] Nucleophilic addition of alkenylzirconocene chloride to aldehydes, which is ordinarily a slow reaction, is remarkably accelerated by a catalytic amount of AgClO.[4] The intermediate species of this reaction is a cationic species.[5b] Although several reports related to the reaction of zirconocene species with aldehydes have appeared, reactions of readily available dialkylzirconocene compounds **3** have not been developed. Indeed, repeated attempts to observe the reaction of Cp_2ZrMe_2 with aldehydes have been uniformly unsuccessful.



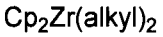
1

allylic zirconocene species



2

cationic zirconocene species



3

dialkyl zirconocene species

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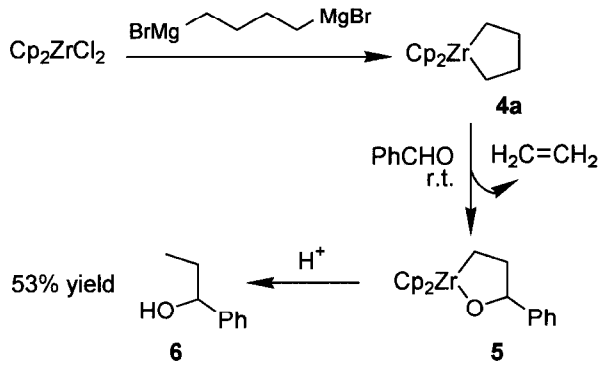
We have reported a reaction of cyclic dialkylzirconocene compound, zirconacyclopentane, with aldehydes.[6] This reaction afforded five-membered oxazirconacyclopentanes *via* β,β′-C-C bond cleavage as shown in Scheme 1.[2e] Insertion of aldehydes with the Zr—C bond was not observed.

Scheme 1

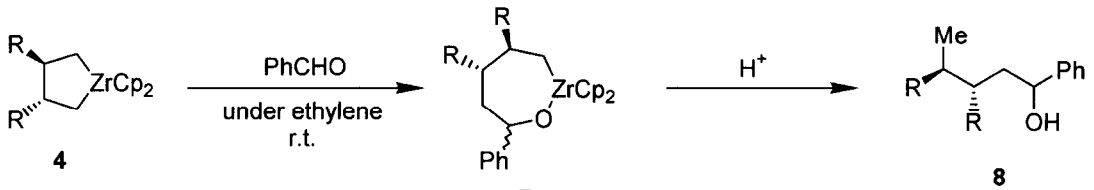


During the course of our investigation into methodologies for selective preparation of zirconacycles, we found that under a slightly positive pressure of ethylene gas, alkynes could react with ethylene with high pair-selectivity to afford zirconacyclopentenes. An excess of ethylene played a very important role in these reactions.[7] This observation prompted us to investigate reactions of zirconacyclopentanes with aldehydes under a slightly positive pressure of ethylene gas. Interestingly, aldehydes inserted into zirconacyclopentanes affording seven-membered oxazirconacycloheptanes.[8] This was the first example of such kind reactions. In this paper, we would like to report this reaction in detail.

Results and discussion

Reaction of zirconacyclopentane **4a**, prepared *in situ* from the reaction of Cp_2ZrBu_2 with an excess of ethylene, with benzaldehyde under a slightly positive pressure of ethylene gas afforded a 7-membered oxazirconacycle **7a** in 70% NMR yield as shown in Scheme 2.[8] The ^{13}C NMR spectrum of **7a** indicated that there were two singlets at δ 117.07 and δ 110.08 assignable to the two Cp rings. The methylene carbon attached to Zr and the carbon of CH attached to oxygen appeared at δ 43.50 and δ 85.70, respectively. Hydrolysis of the above reaction mixture afforded **8a** in 46% isolated yield. Reaction of the substituted zirconacyclopentane **4b**, β,β′-diethyl zirconacyclopentane prepared *in situ* from the reaction of Cp_2ZrBu_2 with 1-butene,[9] with benzaldehyde led to the formation of **8b** in 52% yield after hydrolysis with 3 mol·L^{-1} HCl.

Scheme 2



4a: R = H
4b: R = Et

7a: 70% NMR yield

8a: R = H
8b: R = Et

Bicyclic zirconacyclopentane derivatives **9**, **11**, **13** and **15** prepared *in situ* from the reaction of Cp_2ZrBu_2 with the corresponding terminal dienes (for **9**: 1,6-heptadiene; for **11**: 1,7-octadiene; for **13**: (*Z*)-4,5-dibutyl-1,4,7-octatriene;[10] for **15**: 4,5,6,7-tetraethyl-(4*Z*, 6*Z*)-1,4,6,9-decatetraene[11]) also reacted with aldehydes. Protonolysis easily afforded the corresponding alcohols **10**, **12**, **14** and **16**, respectively, as shown in Scheme 3. Results are listed in Table 1.

Reactions of monocyclic zirconacyclopentanes with benzaldehyde were also carried out at different reaction temperatures. With temperatures increasing, 5-membered oxazirconacyclic compound **5** increased, meanwhile, the insertion reaction product, the 7-membered oxazirconacycle **7a**, decreased. Similar reactions were carried out for bicyclic zirconacyclopentanes. However, very different results from that of the monocyclic analogues were observed, as shown in Scheme 4. Table 2 summarizes results obtained at different temperatures.

It has been demonstrated that dialkylzirconocenes are very inactive toward aldehydes. Cross coupling reactions of aldehydes with zirconocene-alkene complexes

Scheme 3

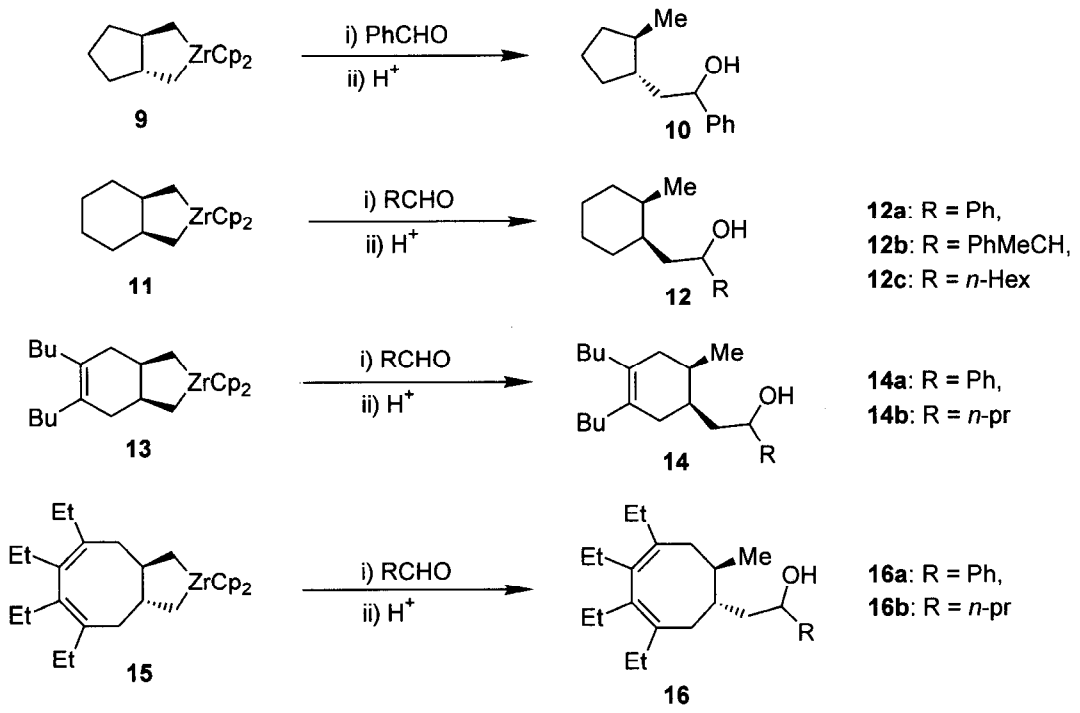


Table 1 Reaction of zirconacyclopentanes with aldehydes followed by protonolysis[a]

Zirconacyclopentane	RCHO	Product	Yield (%)
4a	PhCHO	**8a**	46
4b	PhCHO	**8b**	52[b]
9[c]	PhCHO	**10**	37[d]
11[e]	PhCHO	**12a**	69[f]
11[e]	PhMeCHCHO	**12b**	58[g]
11[e]	$C_6H_{13}CHO$	**12c**	72[h]
13	PhCHO	**14a**	81[i]
13	*n*-PrCHO	**14b**	65[j]
15	PhCHO	**16a**	56
15	*n*-PrCHO	**16b**	45

[a] Isolated yield. In cases when the products are a mixture of diastereomers, a combined yield is shown. [b] A 5:1 diastereomeric-mixture. [c] > 95% *trans*. [d] A3:2 mixture of diastereomers. [e] > 95% *cis*. [f] A 4:3 diastereomeric mixture. [g] A 15:12:5:4 mixture of 4 diastereomers. [h] A 3:2 mixture of 2 diastereomers. [i] A 3:1 mixture of diastereomeric mixture. [j] A 2:1 mixture of 2 diastereomers.

easily take place. Very interesting, cyclic dialkylzirconocene species, zirconacyclopentanes under a slightly positive pressure of ethylene gas reacted with aldehydes to afford the insertion product, the 7-membered oxazirconacyclopentane **7a** as the major product even at room temperature. The 5-membered oxazirconacyclopentane **5** was formed only as the minor product. This reaction presents the first example of aldehyde insertion into one of the Zr-sp^3 carbon bond. Unlike the reaction of zirconocene-diene complex with an aldehyde or a ketone reported by Nakamura and co-workers,[4] 7-membered oxazirconacyclopentanes under an atmosphere of ethylene gas does not react with the second aldehyde. In fact, no double incorporation of aldehyde was observed even when the reaction was carried out in the presence of an excess of aldehydes. These reactions indicated that the reactivity of zirconacyclopentanes toward aldehydes is different from that of allylzirconocene compounds.

Table 2 Reaction of zirconacyclopentanes with **4** and **11** benzaldehyde at different temperatures

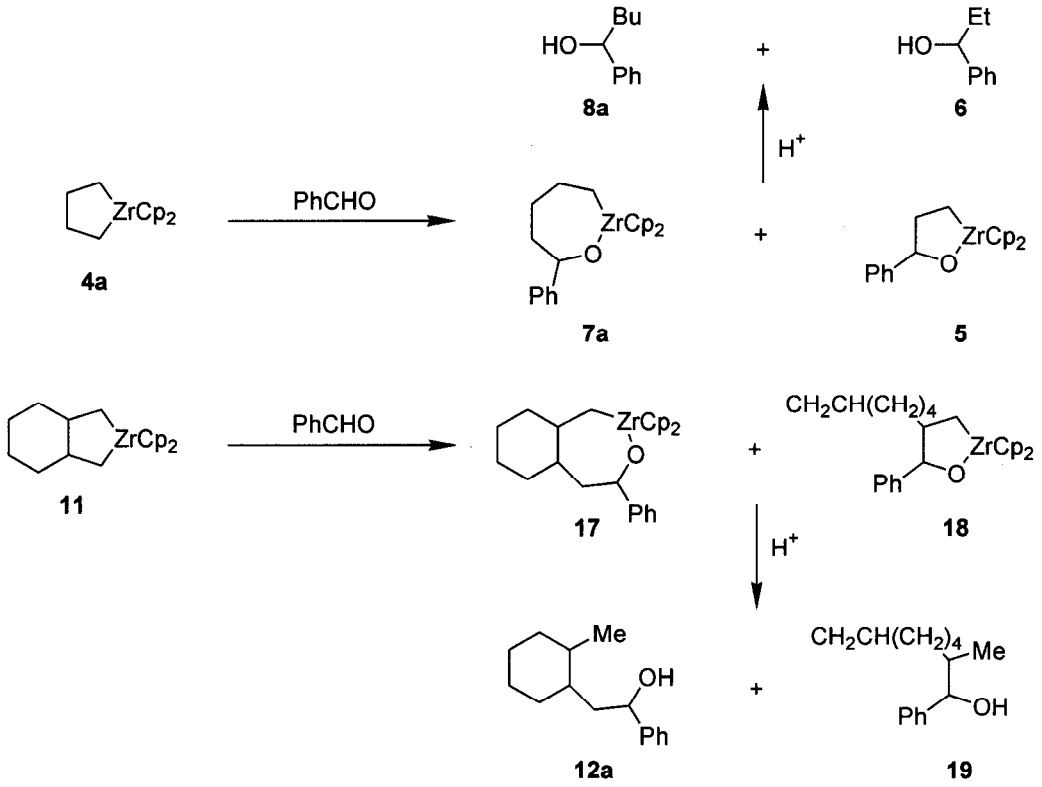
Product	Yield (%)[a]		Yield (%)[b]		Yield (%)[c]	
	1 h	3 h	1 h	3 h	1 h	3 h
8a	52	60	61	62	13	11
6	8	10	12	16	46	54
12a	60	74	62	72	47	52
19	0	0	0	0	0	0

[a] at 0℃, [b] at 20℃, [c] at 50℃.

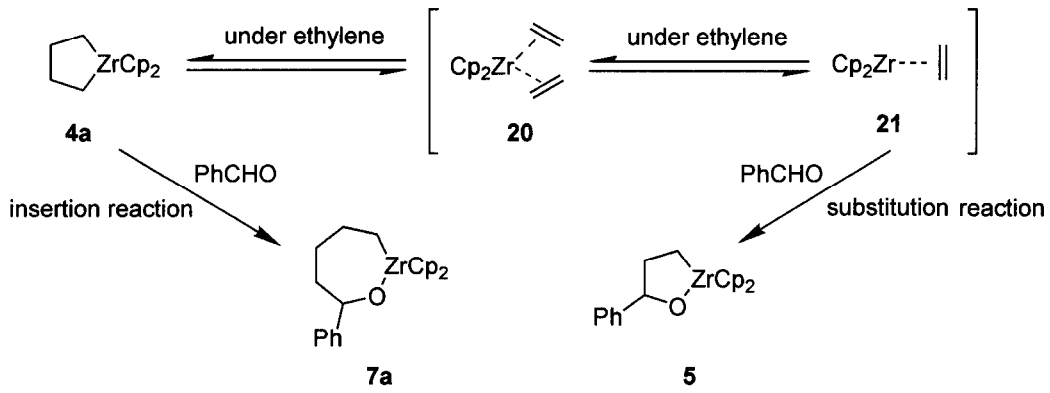
It is obvious that there is a competition between insertion reaction and substitution reaction in case of the monocyclic zirconacyclopentanes, as indicated by results given in Table 2. The presence of an excess of ethylene

contributes to the domination of insertion products, as shown in Scheme 5. Under an atmosphere of ethylene, the excess of ethylene forces the equilibrium going to zirconacyclopentane **4a**. At a higher temperature, β, β′ C—C bond fission reaction becomes faster, leading to the formation of zirconocene-ethylene complex **21**, which rationalizes the observation for the different yields at different temperatures.

Scheme 4



Scheme 5



Acyclic dialkylzirconocene compounds such as dimethylzirconocene do not react with aldehydes. In contrast, cyclic dialkylzirconocene compounds such as zirconacyclopentanes react easily with aldehydes *via* insertion reactions. A possible explanation is that the zirconacyclopentane system has a high tension energy which boosts the reaction with aldehyde. After the energy has been released, the oxazirconacycle is at a stable state which does not react with another aldehyde, thus no double incorporation was observed.

Experimental

Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were carried out under a positive pressure of dry N_2 using standard Schlenk techniques. THF was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc., or from Nichia Chemical Industries, Ltd. Japan. *n*-BuLi and EtMgBr were obtained from Kanto Chemicals Co. Ltd.

GC analysis was performed on a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector using a fused silica capillary column (CBP1-M25-025) and Shimadzu CR6A-Chromatopac integrator. GC yields were determined using suitable hydrocarbons as internal standards. NMR spectra were recorded on a JEOL EX-270 FT NMR spectrometer, or on a JEOL JNM-AL300 FT NMR spectrometer. IR spectra were recorded on Shimadzu FT-IR-4200 spectrometer.

Zirconacyclopentanes **4a**[7b], **4b**[9a], **9**[9b], **11**[9b], **13**[10], **15**[11] were prepared *in situ* according to reported procedures.

Reaction of zirconacyclopentane **4a** *with benzaldehyde under ethylene atmosphere*

Preparation of 1-*phenyl*-1-*pentanol* (**8a**)

To a solution of Cp_2ZrBu_2 formed *in situ* from Cp_2ZrCl_2 (1 equiv) and *n*-BuLi (2 equiv) in THF at −78℃ for 1h was introduced ethylene gas with bubbling at room temperature for 1 h, then, to the reaction mixture under the atmosphere of ethylene gas at 0℃ was added benzaldehyde (1 equiv). The mixture was gradually warmed up to room temperature and stirred for 6 h. Formation of 7-membered oxazirconacycle **7a** (70% NMR yield) was characterized by using NMR. ^{13}C NMR (C_6D_6, TMS) δ: 31.45, 33.21, 36.78, 43.50, 85.70(CH), 110.88(Cp), 111.07(Cp), 125.62, 126.70, 128.35, 147.99. Hydrolysis followed by extracting with ether, washing with brine, concentration and distillation gave the title compound **8a** (stereomeric purity (> 99%) in 46% isolated yield. bp 238—239℃. IR (neat) ν: 700(s), 756(m), 1030(m), 1455(s), 2959(s), 3376(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS) δ: 0.87(t, J = 7.26 Hz, 3H), 1.19—1.42(m, 4H), 1.65—1.80(m, 2H), 2.05—2.16(br, 1H), 4.61(t, J = 7.26 Hz, 1H), 7.28—7.33(m, 5H). ^{13}C NMR ($CDCl_3$, TMS) δ: 14.02, 22.60, 27.98, 38.81, 74.66, 125.98, 127.44, 128.41, 144.97. HRMS calcd for $C_{11}H_{16}O$ 164.1201, found: 164.1201.

A general procedure for the preparation of compounds **8b**, **10**, **12**, **14**, *and* **16**

To a solution of Cp_2ZrBu_2 formed *in situ* from Cp_2ZrCl_2(1 equiv) and *n*-BuLi (2 equiv) in THF at −78℃ for 1 h was added a diene (1 equiv) or 2-butene (2.2 equiv). The reaction mixture was then warmed up to room temperature and stirred for 3 h. After aldehyde (1 equiv) was added, the mixture was stirred at room temperature for 6 h, then quenched with 3 mol·L^{-1} HCl and worked up. Tube-to tube distillation or flash chromatograph was used to purifythose products obtained. When two more equivalents were used, same results as those with one equivalent of aldehyde were obtained for all cases. No double incorporation was observed.

3-*Ethyl*-4-*methyl*-1-*phenyl*-1-*hexanol* (**8b**)

This compound was obtained as a 5:1 diastereomeric mixture. Combined isolated yield was 52%. IR (neat) ν: 700(s), 754(m), 1010(m), 1454(s), 2961(s), 3378(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS) δ: 0.68(t, J = 7.26 Hz, 3H), 0.76(t, J = 6.93 Hz, 3H), 0.85(t, J = 7.86 Hz, 3H), 1.00—1.17(m, 3H), 1.26—1.42(m, 3H), 1.57—1.72(m, 2H), 1.92—2.10(br, 1H), 4.67(t, J = 7.12 Hz, 1H), 7.30—7.33 (m, 5H). ^{13}C NMR($CDCl_3$, TMS) δ for the major: 12.16, 14.75, 24.20, 26.43, 35.54, 39.32, 40.00, 73.80, 126.20, 127.56, 128.41, 144.92; for the minor δ: 12.32, 14.39, 23.77, 26.97, 35.54, 38.78, 39.93, 72.76, 125.73, 127.33, 128.66, 145.74.

2-[(*E*)-2-*Methylcyclopentyl*]-1-*phenyl*-1-*ethanol* (**10**)

To a 3:2 mixture of 2 diastereomers, combined yield was 37%. IR (neat) ν: 700(s), 762(m), 1047(m), 1453(s), 2953(s), 3347(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS) δ for the mixture: 0.80(d, J = 6.93

Hz), 0.98(d, J = 6.27 Hz), 1.26—1.31(m, 4H), 1.52—1.55(m, 2H), 1.69—1.71(m, 2H), 1.85—1.88(m, 1H), 1.92—1.96(m, 1H), 2.21—2.27 (br, 1H), 4.62—4.64 (m, 1H), 7.30—7.33(m, 5H). ^{13}C NMR ($CDCl_3$, TMS) δ for the major: 15.03, 22.35, 29.43, 32.13, 39.46, 40.34, 41.00, 73.69, 125.86, 127.42, 128.41, 145.42; for the minor, 18.99, 23.27, 29.43, 33.37, 36.17, 40.02, 44.00, 74.21, 125.73, 127.33, 128.41, 145.55. HRMS calcd for $C_{14}H_{20}O$ 204.1514, found: 204.1524.

2-[(*Z*)-2-*Methylcyclohexyl*]-*phenyl*-1-*ethanol* (**12a**)

A 4:3 diastereomeric mixture with combined isolated yield 69%. IR(neat) ν: 700(s), 760(m), 1030 (m), 1451(s), 2963 (s), 3345(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS) δ for the mixture: 0.83—0.87(m, 3H), 1.26—1.44(m, 8H), 1.50—1.71(m, 4H), 1.80—1.86(br, 1H), 4.70—4.75(m, 1H), 7.33—7.35 (m, 5H). ^{13}C NMR($CDCl_3$, TMS) δ for the major: 14.48, 22.30, 24.65, 27.26, 32.33, 33.14, 36.12, 41.55, 72.24, 125.80, 127.44, 128.46, 145.55; for the minor, 13.91, 21.98, 25.18, 28.21, 31.61, 32.54, 36.39, 41.55, 72.69, 125.90, 127.51, 128.46, 145.54. HRMS calcd for $C_{15}H_{22}O$ 218.1671, found:218.1669.

4-[(*Z*)-2-*Methylcyclohexyl*]-2-*phenyl*-3-*butanol* (**12b**)

A 15: 12: 5: 4 diastereomeric mixture with combined yield 58%. IR(neat) ν: 700(s), 762(m), 1010 (m), 1452(s), 2961(s), 3370(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS) δ for themixture: 0.68(d, J = 6.94 Hz), 0.77(d, J = 6.94 Hz), 0.78(d, J = 7.00 Hz), 0.83(d, J = 7.00 Hz), 1.20—1.34(m, 8H), 1.35—1.43(m, 2H), 1.65—1.86(m, 3H), 2.70—2.72(m, 1H), 3.68—3.70(m, 1H), 7.18—7.32(m 5H). ^{13}C NMR ($CDCl_3$, TMS) δ for the biggest: 14.65, 15.44, 22.43, 24.51, 27.06, 32.31, 33.60, 36.06, 37.61, 46.11, 73.64, 126.32, 127.76, 128.39, 144.85; for the smallest, 17.72, 17.97, 21.47, 25.93, 28.64, 30.40, 32.92, 36.37, 37.34, 46.49, 73.75, 126.56, 127.79, 128.19, 143.45.

1-[(*Z*)-2-*Methylcyclohexyl*]-2-*octanol* (**12c**)

A 3:2 diastereomeric mixture with combined isolated yield 72%. IR(neat) ν: 1053(m), 1466(s), 2960 (s), 3360(m) cm^{-1}. ^{1}H NMR($CDCl_3$, TMS) δ for the mixture: 0.74—0.82 (m, 6H), 1.21—1.29 (m, 16H), 1.30—1.35(m, 4H), 1.58—1.60(m, 2H), 1.94—1.96(m, 1H), 3.54—3.56(m,1H). ^{13}C NMR ($CDCl_3$, TMS) δ for the major: 14.11, 14.59, 22.44, 22.66, 24.71, 25.73, 27.33, 29.43, 31.91, 32.43, 33.44, 36.01, 38.36, 40.23, 69.59; for the minor: 13.69, 14.13, 21.89, 22.66, 25.48, 25.62, 28.57, 29.43, 31.43, 31.91, 32.73, 36.46, 38.06, 39.59, 69.86. HRMS calcd for $C_{15}H_{29}O$ (M − 1) 225.2218, found: 225.2216.

2-[4, 5-*Dibutyl*-(*Z*)-2-*methyl*-4-*cyclohexenyl*]-1-*phenyl*-1-*ethanol* (**14a**)

A 3:1diastereomeric mixture with combined isolated yield 81%. ^{1}H NMR($CDCl_3$, TMS) δ for the mixture: 0.74—0.91(m, 9H), 1.28—2.16(m, 21H), 4.69—4.73(m, 1H), 7.21—7.36(m, 5H). ^{13}C NMR($CDCl_3$, TMS) δ for the mixture: 14.03, 14.10, 14.13, 14.72, 22.85, 22.85, 22.89, 30.02, 30.76, 30.89, 31.16, 32.45, 32.60, 33.07, 33.57, 33.73, 36.61, 36.78, 41.11, 72.41, 72.96, 125.70, 125.96, 127.33, 127.46, 128.02, 128.29, 128.38, 128.64, 144.99, 145.52. HRMS calcd C_{23} H_{36} O 328.2766, found: 328.2778.

1-[4, 5-*Dibutyl*-(*Z*)-2-*methyl*-4-*cyclohexenyl*]-2-*pentanol* (**14b**)

A 2:1 mixture of diastereomers with combined isolated yield 65%. ^{1}H NMR ($CDCl_3$, TMS) δ for the mixture: 0.90—0.95 (m, 12H), 1.28—1.50 (m, 16H), 1.69—2.01(m, 9H), 3.66—3.70(m, 1H). ^{13}C NMR ($CDCl_3$, TMS) δ for the mixture: 13.65, 14.09, 14.77, 18.77, 18.85, 22.84, 22.87, 29.71, 30.76, 30.82, 30.88, 31.38, 32.55, 32.62, 32.67, 33.29, 33.34, 33.76, 36.67, 37.05, 39.06, 39.90, 39.98, 40.51, 69.41, 69.76, 128.11, 128.30, 128.48, 128.61. HRMS calcd for $C_{20}H_{38}O$ 294.2923, found: 294.2930.

2-[3,4,5,6-*Trtraethyl*-(*E*)-8-*methyl*-3,5-*cyclooctadienyl*]-1-*phenyl*-1-*ethanol* (**16a**)

This compound was obtained as a single product in

56% yield. ^{1}H NMR ($CDCl_3$, TMS) δ: 0.81(t, J = 7.35 Hz, 6H), 0.97—1.02(m, 11H), 1.23—1.31 (m,1H), 1.71—2.30(m, 14H), 4.77(dd, J = 3.10 Hz, J = 7.35 Hz, 1H), 7.22—7.37(m, 5H). ^{13}C NMR($CDCl_3$, TMS) δ: 12.55, 13.66, 13.79, 21.60, 23.22, 24.20, 24.62, 34.97, 37.00, 38.45, 40.48, 46.03, 72.35, 125.68, 127.28, 128.38, 134.33, 134.80, 136.13, 136.28, 145.55. HRMS calcd for $C_{25}H_{38}O$ 354.2923, found: 354.2928.

1-[3,4,5,6-Trtraethyl-(E)-8-methyl-3,5-cyclooctadienyl]-2-pentanol (**16b**)

This compound was obtained as a single product in 45% yield. ^{1}H NMR ($CDCl_3$, TMS) δ: 0.78—0.83 (m, 6H), 0.91—1.05(m, 15H), 1.26—1.31(m, 18H), 3.71—3.73(m, 1H). ^{13}C NMR ($CDCl_3$, TMS) δ: 12.52, 12.55, 13.66, 13.69, 14.11, 18.98, 21.61, 23.23, 24.25, 24.65, 34.86, 36.82, 38.20, 40.53, 40.88, 43.68, 69.29, 134.33, 134.74, 136.19, 136.28. HRMS calcd for $C_{22}H_{40}O$ 320.3079, found: 320.3082.

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