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A highly efficient and practical preparation of 2,4-pentadienyltitaniums and their γ-selective addition reaction with aldehydes and ketones

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Dedicated to Professor Jean Normant in recognition of his outstanding contribution to organometallic chemistry

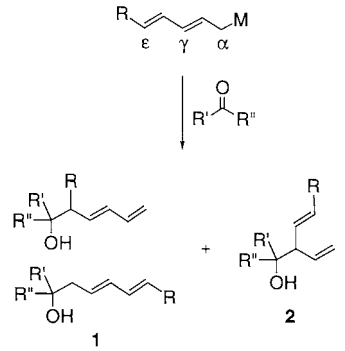
Abstract

A variety of penta-2,4-dienyltitanium complexes including those having a functional group were readily prepared from a divalent titanium reagent, Ti(O–*i*-Pr)$_4$/2*i*-PrMgCl, and penta-1,4-dien-3-ol or penta-2,4-dien-1-ol derivatives, and the organotitaniums thus prepared reacted with aldehydes and ketones smoothly to afford the corresponding penta-1,4-dien-3-yl carbinols highly predominantly in excellent yield.

Keywords: 2,4-Pentadienylmetal; Titanium; 1-(Penta-1,4-dien-3-yl)alkanol; Aldehyde; Ketone; Addition

1. Introduction

Preparation of penta-2,4-dienylmetals and their reaction with aldehydes and ketones have attracted much interest [1]. As shown in Eq. (1), the reaction can give two types of products, i.e. conjugated penta-2,4-dien-1-yl carbinols (**1**) via the reaction at the α- and/or ε-position(s) and non-conjugated penta-1,4-dien-3-yl carbinols (**2**) through the reaction at the γ-position. From the synthetic viewpoint, the greatest concerns in the community of organic chemists have been to achieve easy accessibility to the reagent and to realize high regioselectivity of the reaction. It has been revealed that the regioselectivity can be controlled efficiently by selecting a proper metal reagent. The reagents which show excellent γ-selectivity include the compounds of indium [1w,x], chromium [1f,t], zinc [1a–c,v], silicon [1s], and boron [1j,k,u], and the readiness of access to these reagents varies depending on the metal. Herein, we report that a variety of penta-2,4-dienyltitaniums are readily prepared and that they react with aldehydes and ketones with excellent γ-selectivity.



(1)

Recently, we reported an efficient method for preparing allyltitaniums from a divalent titanium reagent Ti(O–*i*-Pr)$_4$/2*i*-PrMgX (X = Cl or Br) (**3**) [2] and readily available allylic alcohol derivatives such as acetates and carbonates, which proceeds via an oxidative addition pathway [3]. With this result, we were interested in the preparation of penta-2,4-dienyltitaniums from **3** and 1,4-pentadien-3-ol derivatives (**4**) such as ethyl carbonates and acetates and their reaction with aldehydes and ketones (Eq. (2)). As a variety of **4** can be prepared readily, we expected that the reaction might open up an efficient and practical access to a variety of **1** or **2**.

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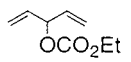
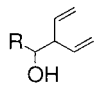
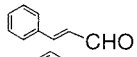
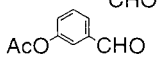
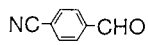
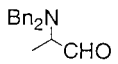
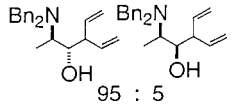
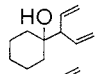
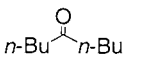
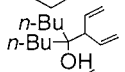
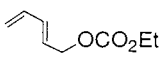
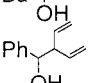
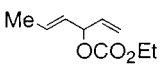
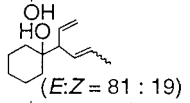
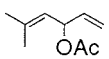
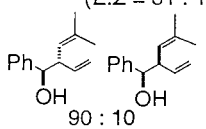
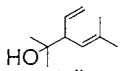
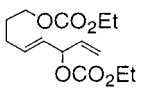
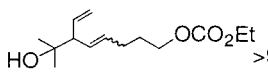
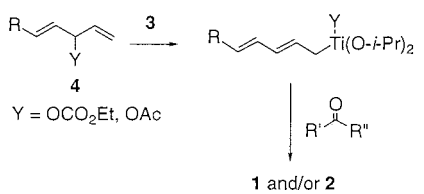
Table 1
Preparation of Penta-2,4-dienyltitaniums from **3** and **4**, and their reaction with aldehydes and ketones [a]

Entry	4	Carbonyl Compound	Product(s)[b] 2	2 : 1[c]	Yield, %[d]
1		RCHO n-$C_7H_{15}CHO$		93 : 7	89
2		PhCHO		99 : 1	81
3				98 : 2	75
4				99 : 1	84
5				99 : 1	82
6			 95 : 5	97 : 3	80
7				96 : 4	92
8				97 : 3	72
9		PhCHO		99 : 1	92
10			 (E:Z = 81 : 19)	>99 : 1	86
11		PhCHO	 90 : 10	>99 : 1	94
12[e]			 santolina alcohol	>99 : 1	82[f]
13[e]			 (E:Z = 87 : 13)	>99 : 1	83[f]

[a]All reactions were carried out using 1.4 equiv. of **4**, 1.5 equiv. of Ti(O-*i*-Pr)$_4$, 3.0 equiv. of *i*-PrMgCl, and 1.0 equiv. of carbonyl compound unless stated otherwise. [b]**1** and **2** could not be separated by column chromatography. [c]Determined by 300 MHz ^{1}H NMR and/or GC analyses. [d]Combined yield of **1** and **2** after column chromatography. [e]The reaction was carried out using 1.0 equiv. of **4**, 1.3 equiv. of Ti(O-*i*-Pr)$_4$, 2.6 equiv. of *i*-PrMgCl, and 1.3 equiv. of acetone. [f]Based on **4**.



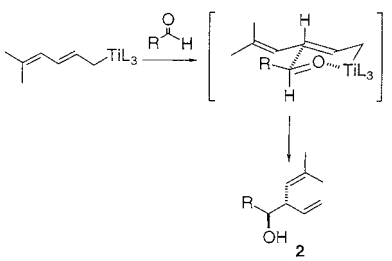
(2)

2. Results and discussion

The results of the preparation of penta-2,4-dienyltitaniums from **3** and **4** and their reaction with a variety of aldehydes and ketones are summarized in Table 1. As can be seen from the table, various kinds of pentadienyltitanium compounds can be prepared readily from the corresponding **4**, and they react with aldehydes and ketones with excellent γ-regioselectivity to afford penta-1,4-dien-3-yl carbinols (**2**) in excellent yield. Several characteristic features can be seen from the table. As a variety of 1,4-pentadien-3-ol derivatives are prepared readily from the corresponding α,β-unsaturated aldehyde and vinyllithium or magnesium compound, we mostly used **4** as the substrate; however, the corresponding 2,4-pentadien-1-ol derivatives can be used

instead of **4** as shown in entry 9 (vs. entry 2). Since an organotitanium reagent shows high chemoselectivity [3,4], it is possible to carry out the reaction with aldehydes and ketones having a functional group (entries 4–6). It is also feasible to prepare functionalized penta-2,4-dienyltitaniums from **4** having a functional group such as ester moiety (entry 13)[1]. Thus, penta-1,4-dien-3-yl carbinols having a variety of functional groups can be readily synthesized in a one-pot reaction. In regard to the diastereoselectivity of the reaction, the reaction of substituted pentadienyltitaniums with aldehydes gave the corresponding but-3-en-1-ol derivatives with *anti*-stereochemistry preferentially (entry 11), as is the case reported for γ-substituted allyltitaniums [3,4]. For the reaction with chiral α-amino aldehydes, the reaction proceeded with high diastereoselectivity as represented by the reaction shown in entry 6 [5].

The predominant production of γ-addition product(s) **2** and the diastereoselectivity observed for the reaction shown in entry 11 can be explained by assuming that the generated allyltitanium would exist mostly as a primary alkyl derivative in order to avoid the steric repulsion, and the addition reaction with carbonyl compounds proceeds through the six-membered chair-like transition structure illustrated in Eq. (3), in which the substituent at the γ-position of the allylic titaniums is in the preferred equatorial position [3,4].



(3)

In summary, we have developed an efficient method for preparing a variety of penta-2,4-dienyltitanium compounds by the reaction of penta-1,4-dien-3-ol or penta-2,4-dien-1-ol derivatives with a Ti(O-*i*-Pr)$_4$/2*i*-PrMgCl reagent, and have found that their addition reaction with aldehydes and ketones proceeds with excellent γ-regioselectivity. As mentioned in the introduction section, a variety of pentadienylmetals which afford selectively penta-1,4-dien-3-yl carbinols by their reaction with carbonyl compounds have been developed. Among them, pentadienylmetals which can be prepared starting from readily available pentadienyl alcohol derivatives are restricted to the chromium compounds [1r][2,3]. As the present reaction can be carried out starting from pentadienyl alcohol derivatives by using inexpensive and non-toxic metallic reagents and the reaction procedure is operationally simple, we believe that the present method is synthetically advantageous over previous methods, and thus, the method might be used widely to prepare various kinds of penta-1,4-dien-3-yl carbinols including those having functional groups[4]. Further investigation on the scope of the present reaction and synthetic utilization of the resulting penta-1,4-dien-3-yl carbinols is underway in our laboratory.

3. Experimental

3.1. General

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively, on a Varian Gemini-2000 spectrometer. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00). IR spectra were recorded on an FT-IR spectrometer (JASCO F'TIIR-230). Elemental analyses were performed on an elemental automatic analyzer. All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Dry solvents (THF and ethyl ether) were purchased from Kanto Chemicals. Ti(O–*i*-Pr)$_4$ was distilled under reduced pressure and was stored under argon. *i*-PrMgCl was prepared from magnesium turnings and *i*-PrCl in ether.

3.2. Preparation of penta-2,4-dienyltitaniums and their reaction with carbonyl compounds

To a solution of ethyl-1,4-pentadien-3-yl carbonate (219 mg, 1.4 mmol) and Ti(O–*i*-Pr)$_4$ (444 μl, 1.5 mmol) in diethyl ether (10 ml) was added *i*-PrMgCl (2.1 ml, 1.43 M in diethyl ether, 3.0 mmol) at −50°C. After stirring at −50 to −40°C for 2 h, to the mixture was added carbonyl compound (1.0 mmol) at −40°C. The resulting mixture was allowed to warm to 0°C over 1 h and then quenched by addition of saturated aqueous $NaHCO_3$ (0.3 ml). After addition of NaF (1.5 g) and Celite (1.5 g), the mixture was filtered through a pad of Celite with diethyl ether. The filtrate was concentrated

[1] For the preparation of allyltitaniums with functional groups, see Refs. [3a,e,f].

[2] Penta-2,4-dienylindium, zinc (and also chromium) compounds were prepared from penta-2,4-dienyl halides, while pentadienylsilanes and boranes were synthesized from pentadienyllithiums or potassiums via transmetallation reaction. See Ref. [1].

[3] The reductive coupling of pentadienyl acetates with carbonyl compounds using a Pd(0)–SmI_2 reagent has been reported; however, the regioslectivity is moderate and is highly dependent on the structure of the substrates, see Ref. [1n].

[4] For examples of utilization of penta-1,4-dien-3-yl carbinols in organic synthesis: Refs. [1o,u,v,x] and refs. cited therein.

in vacuo to give a crude residue, which was analyzed by ^{1}H-NMR and GC to determine the ratio of regioisomers. The residue was subjected to column chromatography on silica gel (hexanes/diethyl ether) to give a mixture of **1** and **2**. The combined yield and ratio of the resulting **1** and **2** are indicated in Table 1. In the case of the reaction for entries 12 and 13 in Table 1, the reaction was carried out using **4** (1.0 mmol), Ti(O–*i*-Pr)$_4$ (1.3 mmol), *i*-PrMgCl (2.6 mmol), and acetone (1.3 mmol), and the yield indicated in the table is based on **4**.

The ^{1}H- and ^{13}C-NMR data of the resulting adducts, 3-vinylundec-1-en-4-ol (entry 1) [1w], 4-phenyl-3-vinylbut-1-en-4-ol (entries 2 and 9) [1s,w], and (*E*)-6-phenyl-3-vinylhex-1,5-dien-4-ol (entry 3) [1s], were in good agreement with those reported.

3.2.1. 1-(3-Acetoxyphenyl)-2-vinylbut-3-en-1-ol (entry 4, Table 1)

The aldehyde was added as a solution in ether to the mixture of the pentadienyltitanium. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.27 (br 5, 1H, OH), 2.29 (s, 3H, CH3), 3.08 (q, $J = 7.2$ Hz, 1H, allylic proton), 4.62 (d, $J = 6.3$ Hz, 1H, CHO), 5.03 (dt, $J = 17.4$, 1.5 Hz, 1H, CH=CH_2), 5.08 (dt, $J = 9.0$, 1.2 Hz, 1H, CH=CH_2), 5.16 (ddd, $J = 1.2$, 1.8, 17.1 Hz, 1H, CH=CH_2), 5.23 (ddd, $J = 1.0$, 1.5, 10.5 Hz, 1H, CH=CH_2), 5.71 (ddd, $J = 7.2$, 10.5, 17.4 Hz, 1H, CH=CH_2), 5.83 (ddd, $J = 8.1$, 10.5,17.4 Hz, 1H, CH=CH_2), 7.00 (ddd, $J = 0.9$, 2.1, 9.0 H, 1H, Ar), 7.07 (t, $J = 4.2$ Hz, 1H, Ar), 7.17 (d, $J = 7.5$ Hz, 1H, Ar), 7.34 (t, $J = 8.0$ Hz, 1H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) 6 20.9, 55.8, 75.6, 117.3, 118.3, 120.0, 120.6, 124.3, 129.0, 136.4, 136.6, 143.9, 150.6, 169.5; IR (neat) 3473, 3077, 2979, 2876, 2064, 1766, 1635, 1610, 1590, 1486, 1444, 1371, 1207, 1139, 1015, 917, 799, 750, 700 cm^{-1}. Anal. Calc. for $C_{14}H_{16}0_3$: C, 72.39; H, 6.94. Found: C, 72.08; H, 7.26%.

3.2.2. 1-(4-Cyanophenyl)-2-vinylbut-3-en-1-ol (entry 5, Table 1)

The aldehyde was added as a solution in THF to the mixture of the pentadienyltitanium. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.36 (d, $J = 2.7$ Hz, 1H, OH), 3.05 (q, $J = 7.5$ Hz, 1H, allylic CH), 4.67 (dd, $J = 2.7$, 6.6 Hz, 1H, CHO), 4.96–5.27 (m, 4H, CH=CH_2), 5.69 (ddd, $J = 7.2$, 10.2, 17.4 Hz, 1H, CH=CH_2), 5.81 (ddd, $J = 8.4$, 10.2, 18.3 Hz, 1H, CH=CH_2), 7.43 (d, $J = 8.1$ Hz, 2H, Ar), 7.63 (d, $J = 8.1$ Hz, 2H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) 656.2, 75.3, 111.2, 117.9, 118.9, 119.1, 127.6, 131.9, 135.7, 136.0, 147.3; IR (neat) 3468, 3078, 3005, 2979, 2878, 2228, 1925, 1845,1635, 1609, 1504, 1412, 1301, 1198, 1046, 998, 921, 835, 763, 684 cm^{-1}. Anal. Calc. for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.06; H, 6.75; N, 7.08%.

3.2.3. 5-(N,N-Dibenzyl)amino-3-vinylhex-1-en-4-ol (entry 6, Table 1)

The diastereo ratio was determined by ^{1}H-NMR analysis based on peak intensity of methyl protons [major: δ 1.11 (d, $J = 6.6$Hz) vs. minor: δ 1.14 (d, $J = 6.9$Hz)] to be 95:5. The stereochemistry was speculated in analogy with the reported reactions of α-amino aldehydes with allyl and propargylorganometallic reagents [5]. Colorless oil. Data for the major (*anti*-)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.11 (d, $J = 6.6$ Hz, 3H, CH_3), 2.84 (quintet, $J = 6.6$ Hz, 1H, CHN), 3.10–3.23 (m, 1H, allylic CH), 3.43 and 3.76 (2d, $J = 13.8$ and 13.8 Hz, CH_2Ph), 3.68 (dd, $J = 4.8$, 5.1 Hz, 1H, CHO), 4.82–5.07 (m, 4H, CH=CH_2), 5.53 (ddd, $J = 7.8$, 10.5,17.4 Hz, 1H, CH=CH_2), 5.69 (ddd, $J = 7.8$, 10.5, 17.1 Hz, 1H, CH=CH_2), 7.15–7.42 (m, 1OH, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$) 6 8.1, 50.5, 54.4, 54.5, 75.0, 116.1, 118.0, 126.8, 128.2, 129.0, 136.2, 138.2, 140.3; IR (neat) 3456, 3062, 3026, 2975, 2931, 2803, 1946, 1810, 1701, 1636, 1601, 1493, 1453, 1376, 1243, 1143, 1072, 1027,1001,916,747,698 cm^{-1}. Anal. Calc. for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 81.90; H, 8.54; N, 4.60%.

3.2.4. 1-(Penta-1,4-dien-3-yl)cyclohexan-1-ol (entry 7, Table 1)

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.05–1.80 (m, 1OH, 5 × CH_2), 2.73 (t, $J = 8.6$ Hz, 1H, allylic proton), 5.04–5.20 (m, 4H, CH=CH_2), 5.92 (ddd, $J =$ 8.6, 10.5, 18.9 Hz, 2H, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) 621.6, 25.6, 35.0, 59.5,72.2, 117.3, 137.0; IR (neat) 3462, 3074, 2933, 2668, 1830, 1634, 1448, 1354, 1263, 1135, 1038, 1001, 963, 914, 803, 759, 691 cm^{-1}. Anal. Calc. for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.80; H, 10.57%.

3.2.5. 5-(Penta-1,4-dien-3-yl)nonan-5-ol (entry 8, Table 1)

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91 (t, $J = 7.1$ Hz, 6H, CH_3), 1.17–1.60 (m, 12H, CH_2), 2.88 (t, $J = 8.4$ Hz, 1H, CH), 5.05–5.17 (m, 4H, CH=CH_2), 5.93 (ddd, $J = 8.4$, 10.2, 18.6 Hz, 2H, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0, 23.2, 25.2, 36.5, 56.4, 75.0, 117.0, 137.3; IR (neat) 3477, 3074, 2956, 2935, 2871, 1828, 1633, 1465, 1415, 1378, 1341, 1260, 1126, 1001, 912, 812, 731, 687 cm^{-1}. Anal. Calc. for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.52; H, 12.46%.

3.2.6. 1-(Hexa-1,4-dien-3-yl)cyclohexan-1-ol (entry 10, Table 1)

Colorless oil. The olefinic stereoisomers could not be separated by column chromatography. For the (*E*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.05–2.00 (m, 1OH, CH_2), 1.71 (d, $J = 4.5$ Hz, 3H, CH_3), 2.62–2.72 (m, 1H, CH), 5.02–5.14 (m, 2H, CH=CH_2), 5.44–5.57

(m, 2H, CH=CH), 5.89(ddd, $J = 8.7$, 10.2, 18.9 Hz, 1H, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.1, 21.6, 21.7, 25.7, 34.9, 35.0, 58.5, 72.3, 116.6, 128.2, 129.3, 137.7. Selected peaks for the (*Z*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.08 (t, $J = 9.0$ Hz, 1H, CH), 5.42–5.69 (m, 2H, CH=CH), 5.86 (ddd, $J = 7.8$, 10.8, 18.9 Hz, 1H, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 34.5, 52.5, 73.0, 126.4, 128.5, 137.3. IR (neat) 3462, 2933, 2856, 1635, 1448, 1375, 1262, 1135, 998, 970, 911, 835 cm^{-1}. Anal. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.56; H, 11.12%.

3.2.7. 1-Phenyl-2-vinyl-4-methylpent-3-en-1-ol (entry 11, Table 1)

Diastereomeric ratio was determined to be 90:10 by ^{1}H-NMR analysis. Colorless oil. (*R**,*S**)-isomer (major diastereomer: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.34 (d, $J = 1.2$ Hz, 3H, CH_3), 1.61 (d, $J = 1.5$ Hz, 3H, CH_3), 2.23 (d, $J = 3.3$ Hz, 1H, OH), 3.18–3.32 (m, 1H, CH), 4.50 (dd, $J = 3.3$, 7.5 Hz, 1H, CHO), 5.03 (br d, $J = 9.6$ Hz, 1H, CH=$C(CH_3)_2$), 5.10–5.20 (m, 2H, CH=CH_2), 5.72–5.87 (m, 1H, CH=CH_2), 7.20–7.40 (m, 5H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.7,25.7, 51.5, 76.4, 116.9, 122.2, 126.8, 127.3, 127.9, 134.5, 138.1, 142.3. Selected peaks for (*R**,*R**)-isomer (minor diastereomer): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.64–4.80 (m, 1H, CHO), 5.62 (ddd, $J = 6.6$, 10.5, 17.2 Hz, 1H, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) 6 73.3, 116.0, 122.3, 136.5, 137.5, 142.1. IR (neat, a mixture of diastereomers) 3419, 3029, 2969, 2913, 2728, 1944, 1810, 1671, 1635, 1493, 1453, 1375, 1194, 1027, 915, 843, 761, 700 cm^{-1}. Anal. Calc. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.15; H, 8.74%.

3.2.8. 2,5-Dimethyl-4-vinylhex-2-en-5-ol (santolina alcohol) [6] (entry 12, Table 1)

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.16 and 1.18 (2s, each 3H, $2 \times CH_3$), 1.66 (d, $J = 1.2$ Hz, 3H, CH_3), 1.76 (d, $J = 1.2$ Hz, 3H, CH_3), 2.98 (dd, $J = 8.7$, 9.9 Hz, 1H, CH), 5.03–5.12 (m, 2H, CH=CH_2), 5.16 (br d, $J = 8.7$ Hz, 1H, CH=$C(CH_3)_2$), 5.72–5.87 (m, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.1, 26.1, 26.5, 26.9, 54.4, 72.5, 116.4, 122.7, 134.9, 138.0; IR (neat) 3421, 3076, 2973, 2929, 1733, 1635, 1455, 1375, 1260, 1139, 998, 912, 849, 786 cm^{-1}.

3.2.9. Ethyl 6-(2-hydroxyprop2-yl)octa-4,7-dien-1-yl carbonate (entry 13, Table 1)

Colorless oil. Data for (*E*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 6H, CCH_3), 1.31 (t, $J = 7.1$ Hz, 3H, CH_2CH_3), 1.62–1.86 (m, 3H, CH_2 and OH), 2.10–2.20 (m, 2H, allylic CH_2), 2.64–2.77 (m, 1H, CH), 4.14 (t, $J = 6.3$ Hz, 2H, OCH_2CH_2), 4.19 (q, $J = 7.1$ Hz, OCH_2CH_3), 5.05–5.16 (m, 2H, CH=CH_2), 5.43–5.60 (m, 2H, CH=CH), 5.85 (ddd, $J = 8.1$, 10.2, 18.6 Hz, 1H, CH=CH_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.2, 26.97, 27.02, 28.2, 28.7, 59.0, 63.7, 66.9, 71.6, 116.8, 129.5, 131.7, 137.4, 154.9. Selected peaks for (*Z*)-isomer: ^{1}H-NMR δ 1.18 (s, 6H, CCH_3), 3.08 (dd, $J = 8.4$, 9.3 Hz, 1H, CH). IR (neat) 3473, 3075 2975, 2935, 1745, 1635, 1466, 1403, 1369, 1262, 1166, 1006, 915, 792 cm^{-1}. Anal. Calc. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.48; H, 9.43%.

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References

[1] (a) F. Gerard, P. Miginiac, Bull. Soc. Chim. Fr. (1974) 1924. (b) F. Gerard, Ph. Miginiac, Bull. Soc. Chim. Fr. (1974) 2527. (c) H. Yasuda, Y. Ohnuma, A. Nakamura, Y. Kai, N. Yasuoka, N. Kasai, Bull. Chem. Soc. Jpn. 53 (1980) 1101. (d) H. Yasuda, M. Yamauchi, A. Nakamura, T. Sei, Y. Kai, N. Yasuoka, N. Kasai, Bull. Chem. Soc. Jpn. 53 (1980) 1089. (e) A. Hosomi, M. Saito, H. Sakurai, Tetrahedron Lett. 21(1980) 3783. (f) T. Hiyama, Y. Okude, K. Kimura, H. Nozaki, Bull. Chem. Soc. Jpn. 55 (1982) 561. (g) D. Seyferth, J. Pornet, J. Org. Chem. 45 (1980) 1721. (h) M. Koreeda, Y. Tanaka, Chem. Lett. (1982) 1299. (i) D. Seyferth, J. Pornet, R.M. Weinstein, Organometallics 1 (1982) 1651. (j) K. Fujita, M. Schiosser, Helv. Chim. Acta 65 (1982) 1258. (k) M.G. Hutchings, W.E. Paget, K. Smith, J. Chem. Res. Synop. (1983) 31; J. Chem. Res. Miniprint (1983) 0342. (l) Y. Naruta, N. Nagal, Y. Arita, K. Maruyama, Chem. Lett. (1983) 1683. (m) W.E. Paget, K. Smith, M.G. Hutchings, G.E. Martin, J. Chem. Res. Synop. (1983) 30; J. Chem. Res. Miniprint (1983) 0327. (n) T. Tabuchi, J. Inanaga, M. Yamaguchi, Tetrahedron Lett. 27 (1986) 1195. (o) L. Ghosez, I. Marko, A.-M. Hesbain-Frisque, Tetrahedron Lett. 27 (1986) 5211. (p) Y. Nishigaichi, A. Takuwa, Chem. Lett. (1990) 1575. (q) Y. Nishigaichi, M. Fujimoto, A. Takuwa, J. Chem. Soc. Perkin Trans. 1(1992) 2581. (r) Y. Nishigaichi, M. Fujimoto, A. Takuwa, Synlett (1994) 731. (s) S. Kobayashi, K. Nishino, J. Org. Chem. 59 (1994) 6620. (t) M. Sodeoka, H. Yamada, T. Shimizu, S. Watanuki, M. Shibasaki, J. Org. Chem. 59 (1994) 712. (u) M. Suginome, Y. Yamamoto, K. Fujii, Y. Ito, J. Am. Chem. Soc. 117 (1995) 9608. (v) M.E. Jung, C.J. Nichols, Tetrahedron Lett. 37 (1996) 7667. (w) T. Hirashita, S. Inoue, H. Yamamura, M. Kawai, S. Araki, J. Organomet. Chem. 549 (1997) 305. (x) S. Woo, N. Squires, A.G. Fallis, Org. Lett. 1(1999) 573. (y) F. Minassian, N. Pelloux-Léon, Y. Vallée, Synlett (2000) 242.

[2] Reviews for synthetic reactions mediated by the titanium(II) reagent: (a) F. Sato, H. Urabe, S. Okamoto, Pure Appl. Chem. 71 (1999) 1511. (b) F. Sato, H. Urabe, S. Okamoto, Synlett (2000) 753. (c) F. Sato, H. Urabe, S. Okamoto, Chem. Rev. 100 (2000) 2835.

[3] (a) A. Kasatkin, T. Nakagawa, S. Okamoto, F. Sato, J. Am. Chem. Soc. 117 (1995) 3881. (b) Y. Gao, F. Sato, J. Org. Chem. 60 (1995) 8136. (c) A. Kasatkin, F. Sato, Angew. Chem. Int. Ed. Engl. 35 (1996) 2848. (d) S. Hikichi, Y. Gao, F. Sato, Tetrahedron Lett. 38 (1997) 2867. (e) X. Teng, A. Kasatkin, Y. Kawanaka, S. Okamoto, F. Sato, Tetrahedron Lett. 38 (1997) 8977. (f) X. Teng, S. Okamoto, F. Sato, Tetrahedron Lett. 39 (1998) 6927. (g) S. Matsuda, D.K. An, S. Okamoto, F. Sato, Tetrahedron Lett. 39 (1998) 7513. (h) X. Teng, Y. Takayama, S.

Okamoto, F. Sato, J. Am. Chem. Soc. 121 (1999) 11961. (i) S. Okamoto, K. Fukuhara, F. Sato, Tetrahedron Lett. 41 (2000) 5561. See also (j) E. Lorthiois, I. Marek, J.F. Normant, J. Org. Chem. 63 (1998) 2442.

[4] (a) M.T. Reetz, Top. Curr. Chem. 106 (1982) 1. (b) D. Seebach, B. Weidmann, L. Widler, in: R. Scheffold (Ed.), Modern Synthetic Methods. Transition Metal in Organic Synthesis, Otto Salle Verlag, Frankfurt and Main, 1983, p. 217. (c) M.T. Reetz, Organotitanium Reagents in Organic Synthesis, Springer–Verlag, Berlin/Heidelberg, 1986.

[5] (a) M.T. Reetz, M.W. Drewes, A. Schmitz, Angew. Chem. Int. Ed. Engl. 26 (1987) 1141. (b) S. Hormuth, H.-U. Reissig, D. Dorsch, Angew. Chem. Int. Ed. Engl. 32 (1993) 1449. (c) T. Hanazawa, S. Okamoto, F. Sato, Org. Lett. 2 (2000) 2369.

[6] Y. Chrétien-Bessière, L. Peyron, L. Bénezet, J. Garnero, Bull. Soc. Chim. Fr. (1968) 2018.