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Preparation of Vinyl Allenes from 1-Lithio-1,3-dienyl Phosphine Oxides and Aldehydes by the Wittig−Horner Reaction

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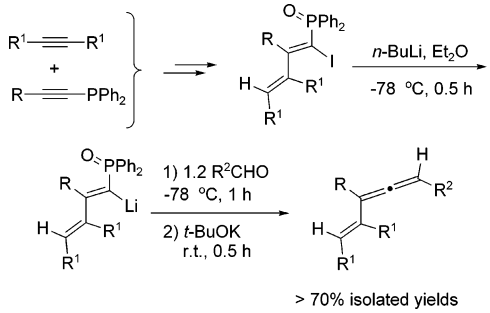

Vinyl allenes were prepared in high yields by the Wittig−Horner reaction of 1-lithio-1,3-dienyl phosphine oxides with aldehydes. 1-Lithio-1,3-dienyl phosphine oxides were generated in situ from lithiation of 1-iodo-1,3-dienyl phosphine oxides, which were obtained by iodination of α-phosphinozirconacyclopentadienes. As a whole, a vinyl allene is synthesized from two different alkynes and one aldehyde.

Introduction

Development of synthetic methods for vinyl allenes has attracted much attention,[1−15] since vinyl allenes, which bear a cumulenic and conjugated vinyl functionality, are useful and unique precursors or intermediates in organic synthesis.[1−15] Several useful methods have been reported, mainly based on reactions of organometallic reagents with suitably functionalized propargyl derivatives.[2−14]

We have recently investigated reactions of 1-lithio-1,3-dienes **1** with unsaturated substrates.[16] Treatment of 1-lithio-1,3-dienes **1** (X = alkyl, aryl or $SiMe_3$) with aldehydes or ketones afforded stereodefined dienols or

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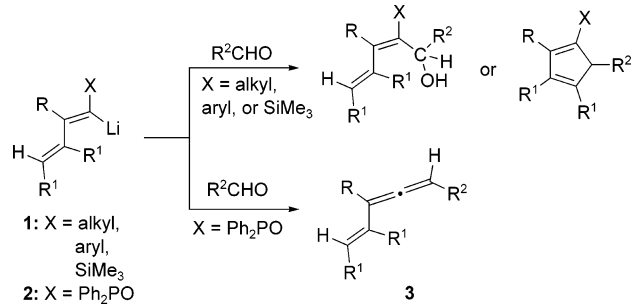
SCHEME 1

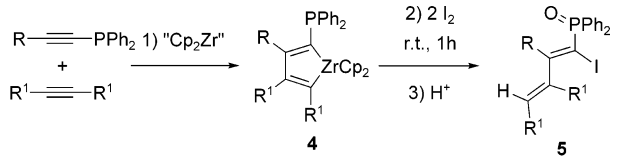


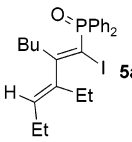
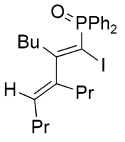
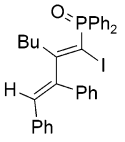
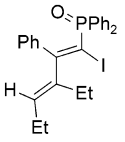
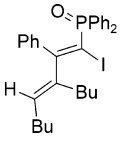
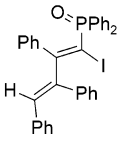
cyclopentadienes (Scheme 1).[17] However, reactions of 1-lithio-1,3-dienyl phosphine oxides **2** (X = Ph_2PO) with aldehydes afforded stereodefined vinyl allenes **3** via the Wittig−Horner reaction.[18,19] In this paper, we report the preparation of vinyl allenes by the Wittig−Horner reaction from 1-lithio-1,3-dienyl phosphine oxides **2** with aldehydes. We also report the scope and limitations of iodination reactions of α-phosphinozirconacyclopentadienes that produce the starting materials 1-iodo-1,3-dienyl phosphine oxides.[20]

Results and Discussion

Preparation of 1-Iodo-1,3-dienyl Phosphine Oxides from Iodination of α-Phosphinozirconacyclopentadienes. Cross-coupling of an alkynylphosphine with a different alkyne took place highly selectively on a low valent zirconocene to afford α-phosphinozirconacyclopentadienes **4**.[20,11] Treatment of **4** with 2 equiv of I_2 afforded 1-iodo-1,3-dienyl phosphine oxides **5** as the only product in moderate isolated yields with high selectivity (Table 1).

TABLE 1. Preparation of 1-Iodo-1,3-dienyl Phosphine Oxides from Two Different Alkynes via α-Phosphinozirconacyclopentadienes



entry	$R-\equiv-PPh_2$	$R^1-\equiv-R^1$	Product **5**	Yield of **5**/%[a]
1	Bu—≡—PPh_2	Et—≡—Et	 **5a**	65
2	Bu—≡—PPh_2	Pr—≡—Pr	 **5b**	61
3	Bu—≡—PPh_2	Ph—≡—Ph	 **5c**	56
4	Ph—≡—PPh_2	Et—≡—Et	 **5d**	39
5	Ph—≡—PPh_2	Bu—≡—Bu	 **5e**	40
6	Ph—≡—PPh_2	Ph—≡—Ph	 **5f**	35

[a] Isolated yields.

Similarly, one Ph_2P- or two Ph_2P-substituted diynes **6** could also be applied to the above reaction. Treatment of a THF solution of Cp_2ZrEt_2 or Cp_2ZrBu_2 with diynes **6** resulted in the formation of the α-phosphinobicyclozirconacyclopentadienes **7**. Hydrolysis with 3 N HCl afforded products **8** in more than 80% isolated yields. As in the case for iodination of the in situ generated intermediate **4**, treatment of **7a** with 2 equiv of I_2 gave the monoiodination product **9a**. The diiodo compound **10a** was formed in good isolated yield when **7a** was first treated with 2 equiv of I_2 and followed by further treatment with 1 equiv of CuCl and 1 equiv of I_2.[21]

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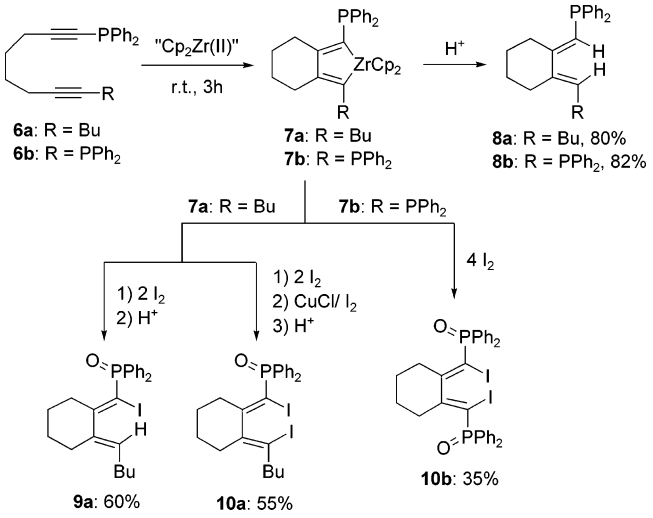
SCHEME 2



However, when **7b** was treated with 2 equiv of I_2, it afforded a mixture of mono- and diiodide products. Treatment of **7b** with 4 equiv of I_2 afforded the diiodo compound **10b** (Scheme 2).

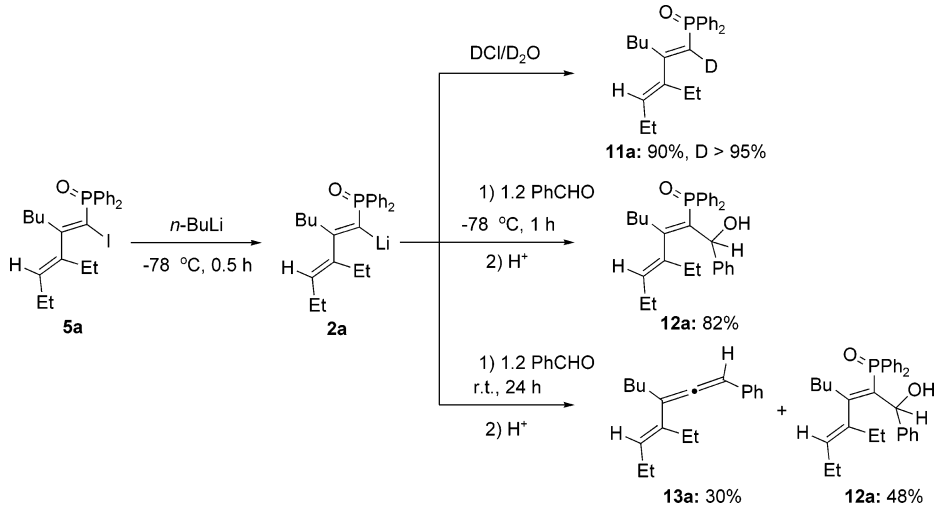
Preparation of Vinyl Allenes from 1-Lithio-1,3-dienyl Phosphine Oxides and Aldehydes. Lithiation of 1-iodo-1,3-dienes with 2 equiv of *t*-BuLi at −78 °C gave their corresponding 1-lithio-1,3-dienes in quantitative yields, as we have already reported.[16,17] Treatment of 1-lithio-1,3-dienes with aldehydes afforded dienols or cyclopentadienes depending on the nature of substituents and hydrolysis conditions.[17] Similarly, 1-lithio-1,3-dienyl phosphine oxide **2a** was prepared by treatment of 1-iodo-1,3-dienyl phosphine oxide **5a** with 1 equiv of *n*-BuLi in Et_2O at −78 °C for 0.5 h. After deuterolysis with 20% DCl in D_2O, **11a** was obtained in 99% GC yield with >95% deuterium incorporation (90% isolated yield). Reaction of **2a** with benzaldehyde at −78 °C for 1 h produced **12a** as a single product in 82% isolated yields after quenching with saturated $NaHCO_3$. When the reaction mixture of **2a** with benzaldehyde was allowed to warm to room temperature for 24 h and quenched with saturated $NaHCO_3$, in addition to **12a**, a vinyl allene **13a** was also obtained in 30% isolated yield (Scheme 3).

These results suggested dienols **12** that came from hydrolysis of intermediate lithium alkoxides **14** and vinyl allenes **13** were formed by spontaneous Wittig−Horner elimination of lithium diphenylphosphinate from **14**.[19] A proposed mechanism for the formation of **12** and **13** is given in Scheme 4. To confirm the formation of intermediate **14**, we treated the isolated alcohol **12a** with *n*-BuLi and *t*-BuOK, and the vinyl allene **13a** was formed in a quantitative yield.

To obtain the vinyl allenes **13** selectively and in high yields, we applied the model reaction of **2a** with benzaldehyde to optimize elimination conditions of lithium diphenylphosphinate from **14**. These results are summarized in Table 2. In the absence of *t*-BuOK, vinyl allene **13a** was formed in 5% isolated yield at room temperature and 76% of **12a** was obtained after hydrolysis (Entry 1). When the reaction time was prolonged, the yield of **13a** increased to 30%. However, when the reaction time was increased to 12 or 24 h, no improvement of the yield of **13a** was observed. These results indicated that the direct conversion of lithium alkoxides **14** to vinyl allenes **13** was not efficient. At the same time, when reaction temperature increased, the reaction was not clean. Therefore, promotion of elimination of lithium alkoxides from **14** was critical for successful preparation of vinyl allenes **13**. Tomioka and co-workers have reported that *t*-BuOK, as a co-base, can work effectively for the activation of lithium alkoxides to afford alkenes.[18e] Therefore, we chose *t*-BuOK as an activating co-base of **14**. When 1 equiv of *t*-BuOK was added to the reaction mixture and the mixture was sirred for 0.5 h at room temperature, the isolated yield of vinyl allene **13a** increased up to 85% as a single product and **12a** was not observed (entry 9). These results indicate that *t*-BuOK, as a strong co-base, can also promote the Wittig−Horner elimination of diphenylphosphinate derivatives from **14**. Use of **9a** and **10a,b** for the Wittig−Horner reaction generated a mixture of products.

Results for the formation of vinyl allenes from 1-lithio-1,3-dienyl phosphine oxides **2** and aldehydes are given in Table 3. The reaction conditions are given in Scheme 5. As shown in Table 3, all aromatic, aliphatic and α,β-unsaturated aldehydes were suitable for the formation of vinyl allenes in more than 70% isolated yields under

SCHEME 3



SCHEME 4

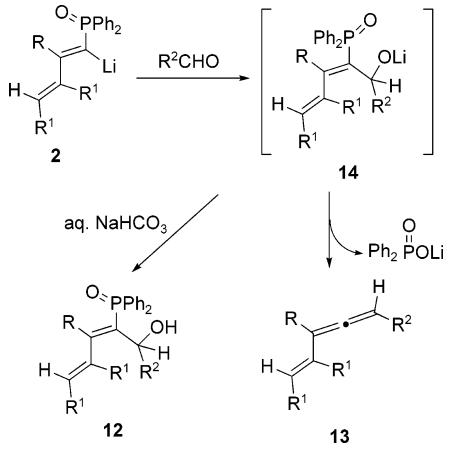
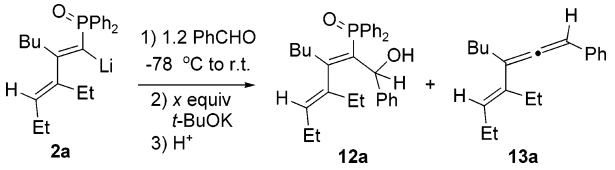


TABLE 2. Elimination Conditions for Formation of Vinyl Allenes



			yields (%)[a]	
entry	equiv of *t*-BuOK	time (h)	**12a**	**13a**
1	0	1	76	5
2	0	2	70	10
3	0	3	60	18
4	0	6	50	25
5	0	12	48	30
6	0	24	48	30
7	0.5	1	25	55
8	0.5	2	0	82
9	1	0.5	0	85

[a] Isolated yields.

the present reaction conditions. At the same time, the substituent R could be an aromatic or aliphatic group. Obviously, this method provides a convenient way to obtain multisubstituted vinyl allenes in high yields by tuning the substituents R and R^1.

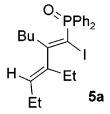
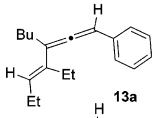
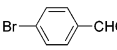
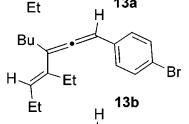
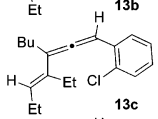
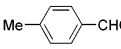
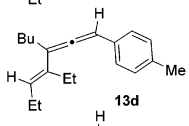
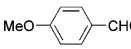
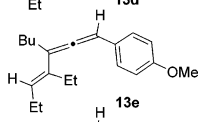
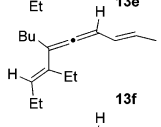
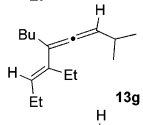
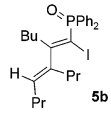
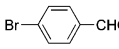
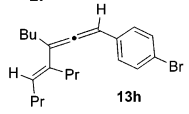
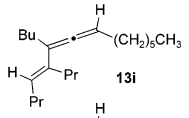
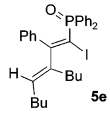
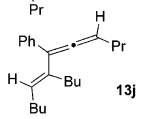
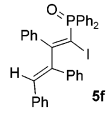
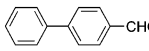
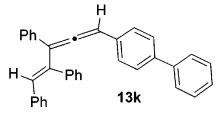
In summary, we have reported a new and convenient method for the preparation of multisubstituted vinyl allenes from 1-lithio-1,3-dienyl phosphine oxides and aldehydes in excellent yields by the Wittig−Horner reaction and widened the scope of iodination reactions of α-phosphinozirconacyclopentadienes. As a whole, the vinyl allene is composed of three molecules including two different alkynes and one aldehyde.

Experimental Section

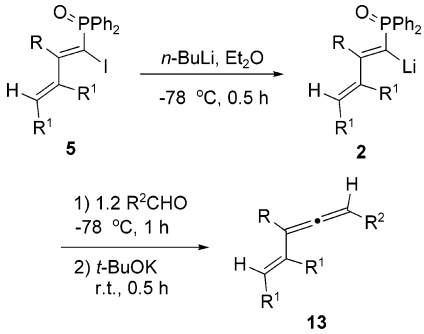
Typical Procedure for Preparation of 1-Iodo-dienyl Phosphine Oxides. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in THF (10 mL) was added EtMgBr (2.5 mmol) at −78 °C. After the mixture was stirred for 1 h at the same temperature, the alkynylphosphine (1.0 mmol) was added and the reaction mixture was allowed to warm to 0 °C for 3 h. The second alkyne (1.0 mmol) was added and stirring was continued at 50 °C for 3 h. After cooling to 0 °C, I_2 (2.0 mmol) was added and stirring was continued at room temperature for 1 h. Then the reaction mixture was quenched with 3 N HCl and extracted with ether. Column chromatography on silica gel afforded 1-iodo-dienyl phosphine oxides.

(1*Z*,3*E*)-2-Butyl-3-ethyl-1-iodo-1,3-hexadienyl(diphenyl)-phosphine Oxide (5a). Light red liquid, isolated yield 65%

TABLE 3. Formation of Vinyl Allenes from 1-Lithio-1,3-dienyl Phosphine Oxide and Aldehydes

Entry	1-iodo-1,3-dienyl phosphine oxides **5**	R^2CHO	Products **13**	Isolated Yield **13**/(%)
1	 **5a**		 **13a**	85
2	**5a**		 **13b**	90
3	**5a**		 **13c**	75
4	**5a**		 **13d**	80
5	**5a**		 **13e**	83
6	**5a**		 **13f**	70
7	**5a**		 **13g**	48
8	 **5b**		 **13h**	88
9	**5b**	n-$C_6H_{13}CHO$	 **13i**	82
10	 **5e**	n-PrCHO	 **13j**	78
11	 **5f**		 **13k**	75

SCHEME 5



(320 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.76 (t, J = 7.2 Hz, 3H), 1.01−1.30 (m, 12H), 2.09−2.18 (m, 2H), 2.26 (q, J = 7.2 Hz, 2H), 5.16 (t, J = 7.2 Hz, 1H), 7.44−7.85 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.7, 13.7, 13.8, 20.9, 22.3, 22.4, 30.7, 34.6 (d, $^3J_{PC}$ = 5.6 Hz), 91.8 (d, $^1J_{PC}$ = 87.8 Hz), 128.2 (d, $^2J_{PC}$ = 12.4 Hz), 131.5 (d, $^4J_{PC}$ = 1.2 Hz), 131.8 (d, $^4J_{PC}$ = 2.5 Hz), 132.3 (d, $^3J_{PC}$ = 9.3 Hz), 133.5 (d, $^1J_{PC}$ = 108.8 Hz), 144.9 (d, $^3J_{PC}$ = 14.4 Hz), 173.2 (d, $^2J_{PC}$ = 6.8 Hz); HRMS calcd for $C_{24}H_{30}OPI$ 492.1079, found 492.1084.

Typical Procedure for Preparation of 8a and 8b. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in THF (10 mL) was added EtMgBr (2.5 mmol) or *n*-BuLi (2.5 mmol) at −78 °C. After the mixture was stirred for 1 h at the same temperature, the diynes (1.0 mmol) was added and the reaction mixture was allowed to warm to room temperature for 3 h to give the α-phosphinobicyclozirconacyclopentadienes **7**. Then the reaction mixture was quenched with 3 N HCl and extracted with ether followed by normal workup to afford crude products, which were purified by column chromatography on silica gel.

(2-Pentylidene-cyclohexylidenemethyl)-diphenyl-phosphane (8a). Colorless viscous liquid, isolated yield 80% (279 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 3H), 1.31−1.65 (m, 8H), 2.04 (q, J = 7.2 Hz, 2H), 2.28−2.60 (m, 4H), 5.54 (t, J = 7.2 Hz, 1H), 6.03 (s, 1H), 7.26−7.42 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 22.4, 26.2, 26.6 (d, $^4J_{PC}$ = 1.2 Hz), 27.3, 28.7, 31.9, 32.6 (d, $^3J_{PC}$ = 24.1 Hz), 119.4 (d, $^1J_{PC}$ = 6.8 Hz), 125.1, 128.1, 128.3 (d, $^3J_{PC}$ = 6.8 Hz), 132.6 (d, $^2J_{PC}$ = 18.5 Hz), 140.0 (d, $^1J_{PC}$ = 9.3 Hz), 141.9 (d, $^3J_{PC}$ = 6.8 Hz), 159.1 (d, $^2J_{PC}$ = 24.1 Hz); HRMS calcd for $C_{24}H_{29}P$ 348.2007, found 348.2009.

Preparation of 9a, 10a, and 10b. The α-phosphinobicyclozirconacyclopentadienes **7a** or **7b** were prepared according to the above-mentioned procedure. **7a** was treated with I_2 (2 mmol) for 1 h at room temperature to give **9a**. **7b** was treated with I_2 (4 mmol) for 1 h at room temperature to give **10b**. When **7a** was first treated with I_2 (2 mmol) for 1 h, followed by addition of CuCl (1 mmol) and I_2 (1 mmol) with stirring for 1 h, **10a** was obtained by the normal purification processes.

Iodo-(2-pentylidene-cyclohexylidene)-methyl(diphenyl)phosphine Oxide (9a). Light red viscous liquid, isolated yield 60% (294 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 6.9 Hz, 3H), 1.37−1.59 (m, 8H), 2.11 (q, J = 6.9 Hz, 2H), 2.33 (t, J = 5.7 Hz, 2H), 3.00−3.04 (m, 2H), 5.35 (t, J = 7.5 Hz, 1H), 7.44−7.84 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 22.5, 27.0, 27.1, 28.0, 29.5, 31.4, 36.9 (d, $^3J_{PC}$ = 6.2 Hz), 85.5 (d, $^1J_{PC}$ = 89.6 Hz), 128.1 (d, $^4J_{PC}$ = 1.9 Hz), 128.3 (d, $^3J_{PC}$ = 12.4 Hz), 131.9 (d, $^4J_{PC}$ = 3.1 Hz), 132.2 (d, $^2J_{PC}$ = 46.4 Hz), 133.6 (d, $^1J_{PC}$ = 108.2 Hz), 144.9 (d, $^3J_{PC}$ = 12.4 Hz), 171.9 (d, $^2J_{PC}$ = 7.4 Hz); HRMS calcd for $C_{24}H_{28}OPI$ 490.0923, found 490.0916.

Iodo-[2-(1-iodopentylidene)cyclohexylidene]methyl-(diphenyl)phosphine oxide (10a). Light red viscous liquid, isolated yield 55% (339 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7.2 Hz, 3H), 1.33−1.63 (br, 6H), 1.82−1.90 (m, 2H), 2.00−3.88 (br, 6H), 7.44−7.98 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 21.8, 28.2, 29.5, 31.3, 33.5, 36.6 (d, $^3J_{PC}$ = 5.6 Hz), 39.8, 89.7 (d, $^1J_{PC}$ = 87.8 Hz), 100.7 (d, $^4J_{PC}$ = 1.9 Hz), 128.1, 128.2, 128.4, 131.9, 132.3 (d, $^2J_{PC}$ = 9.8 Hz), 132.5 (d, $^2J_{PC}$ = 9.3 Hz), 133.6 (d, $^1J_{PC}$ = 5.3 Hz), 151.3 (d, $^3J_{PC}$ = 12.1 Hz), 173.4 (d, $^2J_{PC}$ = 8.7 Hz); HRMS calcd for $C_{24}H_{27}OPI_2$ 615.9889, found 615.9873.

1,2-Bis(1-iodo-1-(diphenylphosphinoyl)methylene)-cyclohexane (10b). Light red solid, isolated yield 35% (266 mg). Mp 152−154 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.58 (t, J = 9 Hz,2H), 1.87−2.22 (m, 4H), 4.06 (d, J = 12 Hz, 2H), 5.29 (s, 2H), 7.41−7.91 (m, 20H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 29.1, 37.3 (d, $^3J_{PC}$ = 4.9 Hz), 53.5, 88.6 (dd, $^1J_{PC}$ = 85.9 Hz, $^4J_{PC}$ = 1.9 Hz), 128.4 (d, $^3J_{PC}$ = 13.0 Hz), 131.0 (d, $^1J_{PC}$ = 109.4 Hz), 132.1 (d, $^1J_{PC}$ = 109.4 Hz), 132.2 132.3 (d, $^3J_{PC}$ = 12.4 Hz), 132.5 (d, $^3J_{PC}$ = 12.4 Hz), 173.4−173.7 (m). Anal. Calcd for $C_{33}H_{30}Cl_2O_2P_2I_2$: C, 46.89; H, 3.58. Found: C, 46.58; H, 3.70. HRMS calcd for $M^+ - CH_2Cl_2$, $C_{32}H_{28}O_2P_2I_2$ 759.9654, found 759.9653.

Typical Procedure for Preparation of 11a and 12a. To an Et_2O (10 mL) solution of **5a** (1.0 mmol) at −78 °C was added *n*-BuLi (1.0 mmol). After this reaction mixture was stirred at −78 °C for 0.5 h and quenched with 20% DCl in D_2O, **11a** was obtained. If a benzaldehyde (1.2 mmol) was added to the above reaction mixture and stirred for 1 h at −78 °C, **12a** was formed after quenching with saturated $NaHCO_3$. Column chromatography on silica gel afforded pure **11a** and **12a**.

(2-Butyl-3-ethyl-1-D-hexa-1,3-dienyl)-diphenyl-phosphine Oxide (11a). Coloress liquid, GC yield 99%, isolated yield 90% (331 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.74 (t, J = 7.2 Hz, 3H), 0.96−1.05 (m, 6H), 1.11−1.24 (br, 4H), 2.12 (q, J = 7.8 Hz, 2H), 2.19−2.29 (m, 2H), 2.63−2.68 (m, 2H), 5.67 (t, J = 7.2 Hz, 1H), 7.40−7.81 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.7, 13.8, 14.2, 21.2, 21.6, 22.7, 31.1, 31.2, 115.7 (d, $^1J_{PC}$ = 104.5 Hz), 128.5 (d, $^2J_{PC}$ = 11.7 Hz), 130.9 (d, $^3J_{PC}$ = 9.9 Hz), 131.2 (d, $^4J_{PC}$ = 3.1 Hz), 132.4, 135.5 (d, $^1J_{PC}$ = 103.2 Hz), 141.7 (d, $^3J_{PC}$ = 16.7 Hz), 166.2 (d, $^2J_{PC}$ = 2.5 Hz); HRMS calcd for $C_{24}H_{30}ODP$ 367.2175, found 367.2177.

3-Butyl-2-(diphenyl-phosphinoyl)-4-ethyl-1-phenyl-hepta-2,4-dien-1-ol (12a). White solid, isolated yield 82% (387 mg). Mp 162−164 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.54−1.14 (br, 13H), 2.06−2.29 (br, 6H), 5.43 (s, 1H), 5.57(s, 1H), 5.93−6.04 (br, 1H), 7.03−7.64 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ13.3, 13.6, 14.1, 21.1, 22.6, 23.3, 29.3, 30.9 (d, $^3J_{PC}$ = 9.3 Hz), 75.4 (d, $^2J_{PC}$ = 7.4 Hz), 126.1, 126.3, 127.6, 128.1 (d, $^2J_{PC}$ = 12.4 Hz), 128.4 (d, $^2J_{PC}$ = 12.4 Hz), 129.7 (d, $^1J_{PC}$ = 93.3 Hz), 131.4 (d, $^3J_{PC}$ = 10.5 Hz), 131.5, 131.8 (d, $^3J_{PC}$ = 10.5 Hz), 132.2, 132.8, 135.7 (d, $^1J_{PC}$ = 100.1 Hz), 138.7 (d, $^2J_{PC}$ = 13.0 Hz), 143.5. Anal. Calcd for $C_{31}H_{37}O_2P$: C, 78.78; H, 7.89. Found: C, 78.62; H, 8.01. HRMS calcd for $C_{31}H_{37}O_2P$ 472.2531, found 472.2546.

Typical Procedure for Preparation of Vinyl Allenes. To an Et_2O (10 mL) solution of 1-iodo-1,3-dienyl phosphine oxide (1.0 mmol) at −78 °C was added *n*-BuLi (1.0 mmol). After this reaction mixture was stirred at −78 °C for 0.5 h, an aldehyde (1.2 mmol) was added and stirred for 1 h at this temperature. Then *t*-BuOK (1 mmol) was added at −78 °C and stirred for 0.5 h at room temperature. The reaction mixture was quenched with saturated $NaHCO_3$ and extracted with ether. Column chromatography on silica gel afforded vinyl allenes.

(3-Butyl-4-ethyl-hepta-1,2,4-trienyl)-benzene (13a). Colorless liquid, isolated yield 85% (216 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H), 1.31−1.52 (m, 4H), 2.12−2.32 (m, 6H), 5.47 (t, J = 7.2 Hz, 1H), 6.33 (s, 1H), 7.13−7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 14.4, 14.5, 21.6, 22.8, 23.1, 29.2, 30.3, 96.8, 111.4, 126.5, 126.6, 127.5, 128.6, 135.5, 136.3, 206.5; HRMS calcd for $C_{19}H_{26}$ 254.2035, found 254.2023.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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