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Stereoselective Synthesis of (Z)- and (E)-1,3-Alkadienes from Aldehydes Using Organotitanium and Lithium Reagents.[1]

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Abstract - [3-(Diphenylphosphino)allyl]titanium reagent generated easily from allyldiphenylphosphine condenses with aldehydes to give (Z)-1,3-alkadienes in a highly regio- and stereoselective manner. In contrast, lithiated allyldiphenylphosphine oxide condenses with aldehydes to give (E)-1,3-alkadienes directly and stereoselectively in good yield. Similarly, lithiated (1-buten-3-yl)diphenylphosphine oxide condenses with aldehydes to give (E)-3-methyl-1,3-alkadienes.

Introduction

The role of the phosphorus function in synthetic organic chemistry has become increasingly apparent.[2] In particular, the α-carbanion stabilized by phosphorus atom is responsible to important developments in olefin synthesis, notable examples of which may be the Wittig reaction[3] and the Wadsworth reaction.[4] Meanwhile, the stereoselective synthesis of 1,3-alkadienes is of great importance in organic chemistry since these compounds often play a role as key synthetic intermediates in natural products synthesis. Thus we intended to develop a new method for the synthesis of 1,3-alkadienes using the conventional phosphorus reagents. Despite the availability of this array of modifications, our experience has been that there are numerous situations in which none of the known processes is really satisfactory.

The reaction of allylic anions containing α-heteroatom substituents has been intensively investigated in recent years and has led to the development of many new synthetic methods.[5] β-Hydroxy organophosphorus compounds, obtained from the reaction of the allyllic anion containing α-phosphorus substituent with carbonyl derivatives, are important class of compounds as they can be selectively converted to 1,3-alkadienes. If it can be possible to obtain these olefinic β-hydroxy phosphorus compounds regio- and diastereoselectively, a general route to stereochemically pure 1,3-alkadienes may be established.

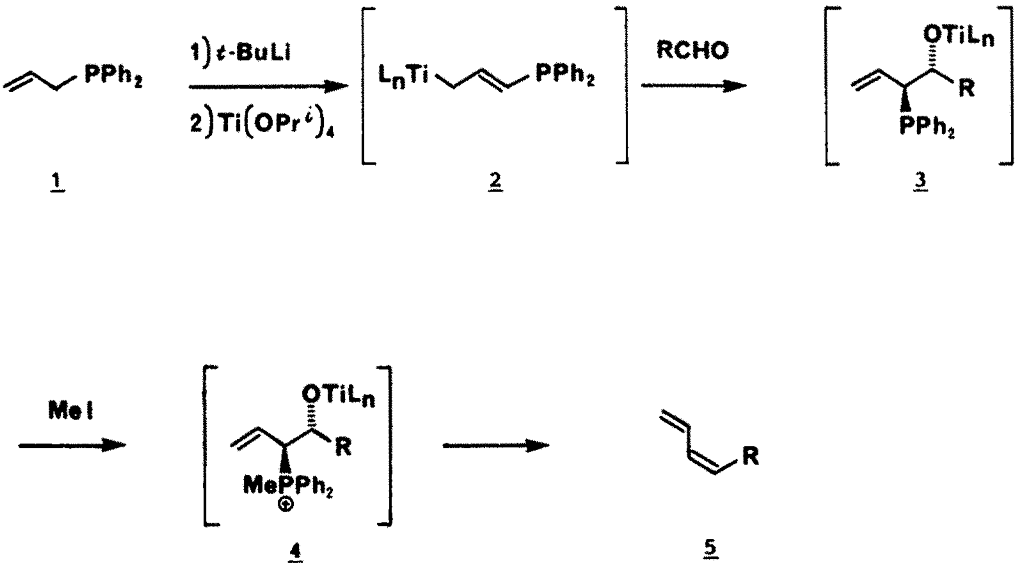
The major problem encountered in the reaction of allylic carbanions with carbonyl compounds is concerned with the regio- (α/γ) and diastereoselectivities (erythro / threo) of the reaction which are rather difficult to control. We have found that this problem has been solved by converting these allylic carbanions into the corresponding organotitanium reagents, which then condensed with aldehydes and ketones with high selectivity.[5,6,7] With these results at hand, we examined the similar reaction of the allylic phosphrus reagent with carbonyl compounds.

Reported herein are highly stereoselective syntheses of [1] (*Z*)-1,3-alkadienes using [3-(diphenylphosphino)allyl]titanium reagent and [2] (*E*)-1,3-alkadienes using lithiated allyldiphenylphosphine oxide from the corresponding aldehydes or ketones. The stereoselective synthesis of (*E*)-3-methyl-1,3-alkadienes using lithiated (1-buten-3-yl)diphenylphosphine oxide is also described.

Results and Discussion

Synthesis of (*Z*)-1,3-Alkadienes. Reaction of [3-(diphenylphosphino)allyl]-titanium reagent of type 2, generated from titanium tetraisopropoxide and the lithiated allyldiphenylphosphine,[8] with aldehydes gave *erythro*-α-adduct 3 exclusively which might be converted without isolation to the β-oxidophosphonium salt of type 4 on treatment with iodomethane.[9] The betaine 4 so produced, was smoothly transformed into the (*Z*)-1,3-diene (5) *via* the cycloelimination of the phosphine oxide, a well-known pathway in the Wittig reaction (Scheme 1).[9] Since the consecutive addition-elimination reaction was usually both satisfactory and convenient, it is advisable not to isolate and purify the intermediary β-hydroxyphosphine. The major results of our findings are illustrated in Table 1.

Scheme 1.



Several trends emerge from these data. The reaction of 2 with aldehydes showed a high regioselectivity to give 1,3-alkadiene (5) in high yield. More remarkable is the high *Z* selectivity of this reaction. The *erythro* 3 should be formed as an intermediate for *syn*-elimination of phosphine oxide gave the (*Z*)-diene. A possible explanation of these trends is as follows.[6] It is generally assumed that the addition of the allylic organometallics to the carbonyl group takes place through allylic rearrangement of the organometallics by a chelated

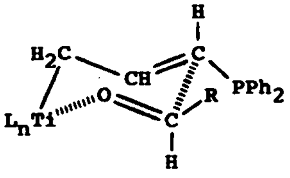
Table 1. Conversion of $R^1R^2C{=}O$ to $\underset{\underline{5}}{R^1R^2C{=}CHCH{=}CH_2}$ using $\underset{\underline{1}}{Ph_2PCH_2CH{=}CH_2}$

Entry	Carbonyl compound	Yield[a]	E / Z[b]
1	Cyclohexanecarbaldehyde	86	4 : 96
2	Decanal	84	5 : 95[c]
3	Perillaldehyde	76	7 : 93
		(33	46 : 54)[d]
4	Benzaldehyde	89	4 : 96
5	(E)-Cinnamaldehyde	82	6 : 94
6	4-t-Butylcyclohexanone	32[e]	-------
7	Acetophenone	29[e]	-------[f]

[a] Yields of isolated product. The products were identified by ^1H NMR and IR spectra, and/or comparison with authentic materials. [b] Unless otherwise specified, E/Z ratio was determined by gc analysis with authentic materials. [c] E/Z ratio was estimated by the NMR assay. [d] Lithiated allyldiphenylphosphine was used. [e] For low reactivity of the titanium reagents, see ref. 7. [f] Not determined.

transition state (Fig. 1). Thus, the structural properties of allylmetal species may considerably reflect on the regioselectivity of the reaction. In other words, the metal site in the organometallic reagents may be the controlling factor of the regioselectivity. If one can accept the allylic rearrangement mechanism, the allyltitanium reagent 2, whose carbon at γ-position of diphenylphosphino group coordinates to titanium, should react with aldehydes at α-position of diphenylphosphino group to give the corresponding α-adduct. It is speculated that this is owing to the steric repulsion between the titanium and the geminal substituent. The observed high Z selectivity of the diene product is explained by considering the transition state structure 6 for the allylic rearrangement (Fig. 1). Both the bulky diphenylphosphino and alkyl group (R) of aldehyde should occupy the equatorial positions in the six-membered ring transition state. Hence the erythro adduct 3 should be formed selectively, which in turn was converted to the (Z)-1,3-alkadiene.

Fig. 1.



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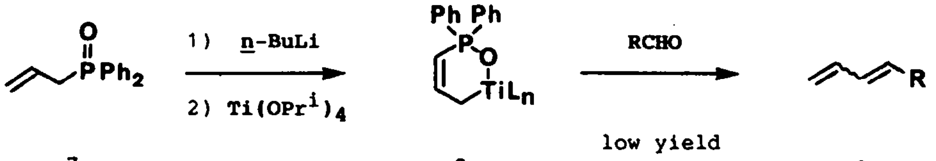
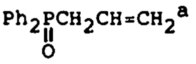
Synthesis of (E)-1,3-Alkadienes and (E)-3-Methyl-1,3-Alkadienes. In order to prove further the generality and limitations of our new process, we turned our attention to the possibility of synthesizing (E)-1,3-dienes by means of readily



7 8 9 (eq. 1)

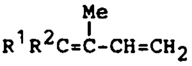
Table 2. Conversion of $R^1R^2C{=}O$ to $R^1R^2C{=}CHCH{=}CH_2$ (**9**) using



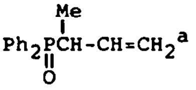
$Ph_2\underset{\underset{O}{\|}}{P}CH_2CH{=}CH_2$[a] **7**

Entry	Carbonyl compound	Yield[b]	*E* / *Z*[c]
1	Cyclohexanecarbaldehyde	82	90 : 10
		(36	94 : 6)[d]
2	Decanal	88	95 : 5[e]
		(25	-------)[f,g]
3	Perillaldehyde	42	94 : 6
4	Benzaldehyde	79	95 : 5
5	4-*t*-Butylcyclohexanone	83	-------

Table 3. Conversion of $R^1R^2C{=}O$ to



$R^1R^2C{=}\overset{\overset{Me}{|}}{C}{-}CH{=}CH_2$ **11** using



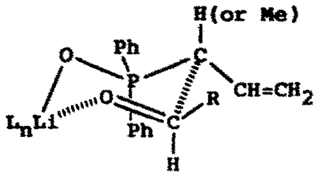
$Ph_2\underset{\underset{O}{\|}}{P}\overset{\overset{Me}{|}}{C}H{-}CH{=}CH_2$[a] **10**

Entry	Carbonyl compound	Yield[b]	*E* / *Z*[c]
1	Cyclohexanecarbaldehyde	64	91 : 9
		(55	85 : 15)[d]
2	Decanal	78	-------[g]
		(42	-------)[f,g]
3	Benzaldehyde	63	93 : 7
		(18	-------)[f,g]
4	4-*t*-Butylcyclohexanone	41	-------

[a] The products were identified by ^1H NMR and IR spectra, and/or comparison with authentic materials. [b] Yields of isolated product. [c] Unless otherwise specified, *E*/*Z* ratio was determined by gc analysis with authentic materials. [d] No HMPA was used. [e] *E*/*Z* ratio was estimated by the NMR assay. [f] Corresponding titanium reagent was used. [g] Not determined.

available allyldiphenylphosphine oxide (7).[10] By analogy with the above results, production of a six-membered ring cyclic intermediate 8, which should be transformed to the (E)-1,3-diene after condensation with aldehydes *via* allylic rearrangement, may be crucial. Unfortunately the titanium derivative from 7 was found to be a totally unsatisfactory reagent for such transformations because of its low reactivity and no or very small amount of 1,3-diene was produced under the similar reaction conditions as those for allylphosphine (eq. 1).[10] Surprisingly, however, when the similar reaction using the lithio derivative from 7 was conducted in THF in the presence of 2 equiv. of hexamethylphosphoric triamide (HMPA) at -78°C for 10 min, followed by stirring at 20°C and isolation, the (E)-1,3-diene (9) was formed predominantly (E/Z ratios in the range 90:10 to 95:5).[11] Similarly, the reaction of (1-buten-3-yl)diphenylphosphineoxide (10) and aldehydes gave (E)-3-methyl-1,3-alkadienes (11) stereoselectively in good yield. The results are illustrated in Table 2 and 3. The high selectivity from this reaction may be explained by considering a possible transition state in Fig. 2, in which substituents such as vinyl of lithium reagent and alkyl group of aldehyde should occupy the equatorial positions, thereby producing the (E)-1,3-dienes selectively.

Fig. 2.



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In conclusion, with a variety of carbonyl compounds, a simple one-pot procedure is now available for the synthesis of (E)- or (Z)-1,3-diene with high stereoselectivity in good yield.

Experimental

General. The IR spectra were determined on a Hitachi 260-10 spectometer in a CCl_4 solution unless otherwise stated. The NMR spectra were recorded on a JNM-PMX 60 spectrometer, using tetramethylsilane as an internal standard. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, and br: broad peak. The isomeric ratio of the products was determined by gas chromatography (gc) on a 25-m PEG-HT capillary column using a Hitachi Model 163 and 164 instruments equipped with a flame ionization detector using nitrogen as carrier gas. The analyses were performed at the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University. Tetrahydrofuran (THF) and ether were distilled from benzophenone ketyl. Benzene, hexane, and toluene were dried over sodium metal. Dichloromethane was dried over 4A molecular sieves. Hexamethylphosphoric triamide (HMPA) was distilled from CaH_2 under reduced pressure. All the experiments were carried out under an argon atmosphere. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Purification of the product was carried out by column chromatography on silica gel Fuji BW-820.

Allyldiphenylphosphine (1) was prepared in 50% yield: bp. 152°C (1.5 Torr).[12]

Synthesis of (Z)-1,3-Alkadienes (5): Reaction of (Diphenylphosphino)allyltitanium Reagent (2) with Carbonyl Compounds. The following experimental procedure provides details of typical reaction conditions. To a solution of 1 (0.54 g, 2.4 mmol) in THF (8 ml) was added a solution of t-butyllithium[8] in pentane (2.4 M, 1.0 ml, 2.4 mmol) dropwise at -78°C. The resulting mixture was stirred at 0°C for 30 min. Titanium tetraisopropoxide (0.71 ml, 2.4 mmol) was added dropwise at -78°C, and the resulting redish solution was stirred at -78°C for 10 min. Cyclohexanecarbaldehyde (0.22 g, 2.0 mmol) was added over a period of 5 min at -78°C to an above solution of allyltitanium reagent (*3*), and the mixture was stirred at -78°C for 10 min and then at 0°C for 1 h. Iodomethane (0.15 ml, 2.4 mmol) was added at 0°C and the mixture was stirred at room temperature for 2 h and then poured into ice-cooled aqueous hydrochloric acid. The product was extracted three times with ether, and the combined organic layers were washed with brine and concentrated. The residual oil was purified by column chromatography on silica gel to give **1-cyclohexyl-(*Z*)-1,3-butadiene** as a colorless oil in 86% yield (0.23 g, 1.7mmol): *E*/*Z* ratio 4:96 by gc, t_R: *Z*-isomer 10.0 min, *E*-isomer 10.7 min at 60°C; R_f= 0.59 (hexane); IR (CCl_4) 3074, 2990, 1645, 1600, 1002, 967, and 910 cm^{-1}; ^1H NMR (CCl_4) = 0.66-2.35 (br, 10H), 2.41 (br m, 1H), 4.85-5.44 (m, 3H), 5.79 (dd, J= 11 and 11 Hz, 1H), 6.57 (ddd, J= 11, 11 and 17 Hz, 1H); Anal. Found: C, 87.90; H, 12.10%. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84%.

(*Z*)-1,3-Tridecadiene was obtained in 84% yield as a colorless oil (*E*/*Z* ratio <5:>95 by the NMR assay): R_f= 0.60 (hexane); IR (neat) 3100-2750, 1805, 1640, 1590, 1460, 1380, 970, 900, 780, and 720 cm^{-1}; ^1H NMR (CCl_4) δ= 0.67-2.50 (br, 19H), 4.86-5.60 (m, 3H), 5.88 (dd, J= 11 and 11 Hz, 1H), 6.53 (ddd, J= 11, 11 and 17 Hz, 1H); Anal. Found C, 86.59; H, 13.41%. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41%.

[(*Z*)-1-Butadienyl]-4-(1-methylethenyl)-1-cyclohexene was obtained in 76% yield as a colorless oil: *E*/*Z* ratio 7:93 by gc, t_R: *E*-isomer 14.7 min, *Z*-isomer 18.7 min at 80°C; R_f= 0.51 (hexane); IR (neat) 2980, 2950, 1660, 1640, 1560, 1260, and 1010 cm^{-1}; ^1H NMR (CCl_4) δ= 1.73-2.60 (m, 10H), 4.70-7.16 (m, 8H); Anal. Found: C, 89.63; H, 10.37%. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41%.

1-Phenyl-(*Z*)-1,3-butadiene was obtained in 89% yield as a colorless oil: E/Z ratio 4:96 by gc, t_R: *Z*-isomer 4.9 min, *E*-isomer 5.9 min at 150°C; R_f= 0.45 (hexane); IR (neat) 3100, 3040, 2980, 2950, 1820, 1640, 1610, 1500, 1455, 1440, 1085, 1040, 1010, 955, 915, 870, 790, 760, and 700 cm^{-1}; ^1H NMR (CCl_4) δ= 4.96-5.49 (br m, 2H), 5.93-7.49 (m, 8H); Anal. Found: C, 92.31; H. 7.69%. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74%.

1-Phenyl-(*E*,*Z*)-1,3,5-hexatriene was obtained in 82% yield as a colorless oil: *E*/*Z* ratio 6:94 by gc, t_R: *Z* isomer 32.2 min, *E* isomer 32.9 min at 150°C; R_f= 0.40 (hexane); IR (neat) 3040, 1810, 1630, 1610, 1500, and 1460 cm^{-1}; ^1H NMR (CCl_4) δ= 4.83-7.50 (m, 12H); Anal. Found: C, 92.19; H, 7.81%. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74%.

4-*t*-Butyl-(2-propenylidene)-1-cyclohexane was obtained in 32% yield as a colorless oil: R_f= 0.56 (hexane); IR (neat) 2950, 1650, 1540, 1365, and 1240 cm^{-1}; ^1H NMR (CCl_4) δ= 0.00-3.00 (16H), 4.93 (d, J= 14 Hz, 1H), 5.07 (d, J= 10 Hz, 1H), 5.65 (d, J= 9 Hz, 1H), 6.47 (ddd, J= 9, 10 and 14 Hz); Anal. Found: C, 87.51; H, 12.49%. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44%.

Allyldiphenylphosphine oxide (*7*): A mixture of allyl alcohol (6.8 ml), chlorodiphenylphosphine (18 ml) and pyridine (18 ml) in ether (200 ml) was stirred at 0°C for 1 h. Powdered $NaHSO_4 \cdot H_2O$ (30 g) was added and stirred for 5 min. The suspension was filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in xylene (100 ml) and the mixture was heated at reflux for 3 h. Concentration followed by recrystallization (ether-hexane) gave *7* in 65-73% yield.[13]

Synthesis of (*E*)-1,3-Alkadienes (*9*): Reaction of (Diphenylphosphoryl)allyllithium with Carbonyl Compounds. The following experimental procedure provides details of typical reaction conditions. To a stirred solution of *7* (0.27 g, 1.2 mmol) in THF (4 ml) and HMPA (0.43 g, 2.4 mmol) was added a solution of *n*-butyllithium in hexane (1.7 *M*, 0.7 ml, 1.2 mmol) dropwise at -78°C. The resulting solution was stirred at -78°C for 10 min. Cyclohexanecarbaldehyde (0.11 g, 1.0 mmol) was added over a period of 15 min, and the resulting solution was stirred at -78°C for 10 min, at 0°C for 30 min and finally at 20°C for 2 h, and then poured into ice-cooled aqueous hydrochloric acid. The product was extracted three times with pentane. The combined organic layers were washed with brine, dried and concentrated. Chromatography of residual oil on silica gel column gave **1-cyclohexyl-(*E*)-1,3-butadiene** as a colorless oil in 82% yield (0.11 g, 0.8 mmol): *E*/*Z* ratio 90:10 by gc): R_f= 0.59 (hexane); IR (neat) 2930, 2850, 1810, 1660, 1610, 1450, 1000, and 900 cm^{-1}; ^1H NMR (CCl_4) δ= 0.73-2.33 (br, 11H), 4.83-6.73 (m, 5H).

(*E*)-1,3-Tridecadiene was obtained in 88% yield as a colorless oil (*E*/*Z* ratio >95:<5 by the NMR assay): R_f= 0.60 (hexane); IR (neat) 2950, 1810, 1665, 1615, 1480, 1270, and 1010 cm^{-1}; ^1H NMR (CCl_4) δ= 4.93 (d, J= 8 Hz, 1H), 5.03 (d, J= 16 Hz, 1H), 5.50 (dt, J= 6 and 14 Hz, 1H), 6.00 (dd, J= 9 and 14 Hz, 1H), 6.30 (ddd,

$J = 8$, 9 and 14 Hz, 1H).

[(*E*)-1-butadienyl]-4-(1-methylethenyl)-1-cyclohexene was obtained in 42% yield as a colorless oil (*E*/*Z* ratio 94:6 by gc): $R_f = 0.51$ (hexane); IR (neat) 2940, 1700, 1637, 1555, 1460, 1005, and 903 cm^{-1}; ^1H NMR (CCl_4) $\delta = 0.73$-2.67 (10H), 4.58-6.53 (m, 8H).

1-Phenyl-(*E*)-1,3-butadiene was obtained in 79% yield as a colorless oil (*E*/*Z* ratio 95:5 by gc): $R_f = 0.44$ (hexane); IR (neat) 3040, 1815, 1615, 1503, 1455, and 1005 cm^{-1}; ^1H NMR (CCl_4) $\delta = 4.97$-7.50 (m, 10H).

4-*t*-Butyl-1-(2-propenylidene)-cyclohexane was obtained in 83% yield and physical data were described above.

3-Diphenylphosphoryl-1-Butene (10) was prepared in 77% yield by the same procedure of the preparation of allyldiphenylphosphine oxide.[13]

Synthesis of 3-Methyl-(*E*)-1,3-Alkadienes (11): Reaction of Lithiated (1-Buten-3-yl)diphenylphosphine oxide with Carbonyl Compounds. To a solution of 10 (0.31 g, 1.2 mmol) in THF (4.0 ml) and HMPA (0.43 g, 2.4 mmol) was added dropwise a solution of *n*-butyllithium in hexane (1.7 *M*, 0.7 ml, 1.2 mmol) at -78°C, and the resulting solution was stirred at -78°C for 10 min. Cyclohexanecarbaldehyde (0.11 g, 1.0 mmol) was added over a period of 15 min at -78°C. The reaction mixture was stirred at -78°C for 10 min, at 0°C for 30 min, finally at 20°C for 2 h, and then poured into ice-cooled aqueous hydrochloric acid. The product was extracted three times with pentane. The combined organic layers were washed with brine, dried and concentrated. Chromatography of residual oil on silica gel column gave **1-cyclohexyl-2-methyl-(*E*)-1,3-butadiene** as a colorless oil in 64% yield (95 mg, 0.6 mmol): *E*/*Z* ratio 91:9 by gc, t_R: *Z*-isomer 8.0 min, *E*-isomer 8.7 min at 80°C; $R_f = 0.81$ (hexane); IR (neat) 2900, 1635, 1595, 1435, 980, and 880 cm^{-1}; ^1H NMR (CCl_4) $\delta = 0.57$-2.93 (14H), 4.77 (d, $J = 10$ Hz, 1H), 4.93 (d, $J = 18$ Hz, 1H), 5.20 (d, $J = 7$ Hz, 1H), 6.20 (dd, $J = 10$ and 18 Hz, 1H); Anal. Found: C, 87.66; H, H, 12.34%. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07%.

3-Methyl-(*E*)-1,3-tridecadiene was obtained in 78% yield as a colorless oil: $R_f = 0.68$ (hexane); IR (neat) 2940, 2860, 1650, 1615, 1550, 1475, 1255, 995, and 875 cm^{-1}; ^1H NMR (CCl_4) $\delta = 0.58$-2.38 (22H), 4.97 (d, $J = 11$ Hz, 1H), 4.98 (d, $J = 17$ Hz, 1H), 5.40 (t, $J = 8$ Hz, 1H), 6.28 (dd, $J = 11$ and 17 Hz, 1H); Anal. Found: C, 86.52; H, 13.48%. Calcd for $C_{14}H_{26}$: C, 86.51; H, 13.49%.

1-Phenyl-2-methyl-(*E*)-1,3-butadiene was obtained in 63% yield as a colorless oil: *E*/*Z* ratio 93:7 by gc, t_R: *Z*-isomer 10.5 min, *E*-isomer 11.9 min at 80°C; $R_f = 0.43$ (hexane); IR (neat) 3100, 2970, 1815, 1605, 1500, 1258, 1000, and 875 cm^{-1}; ^1H NMR (CCl_4) $\delta = 1.93$ (s, 3H), 4.97 (d, $J = 5$ Hz, 1H), 5.23 (d, $J = 13$ Hz, 1H), 6.40 (s, 1H,), 6.43 (dd, $J = 5$ and 13 Hz, 1H), 7.20 (5H); Anal. Found: C, 91.56; H, 8.44%. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39%.

4-*t*-Butyl-1-(1-methyl-2-propenylidene)cyclohexane was obtained in 41% yield as a colorless oil: $R_f = 0.61$ (hexane); IR (neat) 2960, 1725, 1375, 1255, 995, and 875 cm^{-1}. ^1H NMR (CCl_4) $\delta = 0.85$-3.23 (m, 18H), 4.90 (d, $J = 11$ Hz, 1H), 5.07 (d, 17 Hz, 1H), 6.77 (dd, 11 and 17 Hz, 1H); Anal. Found: C, 87.28; H, 12.72%. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.11%.

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