SYNTHESIS OF ALKENYLPHOSPHONIUM SALTS FROM TRIBUTYL[(TRIMETHYLSILYL)METHYLENE]PHOSPHORANE AND ENOLISABLE ALDEHYDES

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Efficient synthesis of alkenylphosphonium salts via treatment of enolizable aliphatic aldehydes with tributyl[(trimethylsilyl)methylene]phosphorane has been described. The simple way for preparation of tributyl[(trimethylsilyl)methylene]phosphorane is also presented.
Keywords: Phosphorus ylides; Rearrangements; Betaines; Alkenylphosphonium salts; Tributyl[(trimethylsilyl)methylene]phosphorane; Peterson olefination; Enolisable aldehydes

The alkenylphosphonium salts have been extensively investigated for the last four decades of the past century and the results of these investigations have been a subject of numerous reviewes[1,2]. These phosphonium salts have found wide application in organic chemistry after it was settled out that their reaction with nucleophiles results in phosphorus ylides, which subsequently may be subjected to produce, via Wittig olefination, carbo- and heterocyclic systems in a stereoselective manner[3]. This powerful methodology was applied in the elegant synthesis of such compounds as *E*- or *Z*-*N*-allylpyrroles[4], tetraalkyl (1*Z*,3*Z*)-buta-1,3-diene-1,2,3,4-tetracarboxylates[5], precursor of (–)-supidine[6] and functionalized coumarins[7]. Alkenylphosphonium salts have been used in the radical addition to give products which were further converted to a variety of useful synthetic intermediates[8], as an electron-deficient dienophile in Diels–Alder cycloaddition[9], and in polymerization to produce antimicrobal polymers[10]. Additionally, triarylalkenylphosphonium salts have been investigated as the potential reagents for radioactive labeling of immunoglobins and other proteins[11].

The alkenylphosphonium salts are conveniently synthesized from the β-substituted alkylphosphonium salts through β-elimination reaction in the presence of a base[12], by the addition of the titanium-substituted ylide spe-

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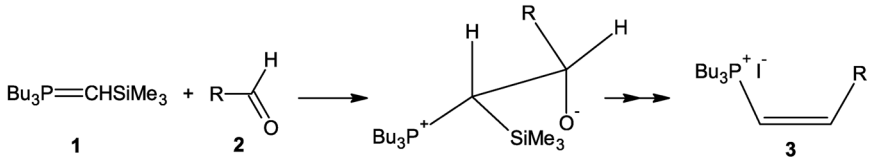
cies to carbonyl compounds[13] or via a stereoselective vinylation of phosphine with vinyl triflates or vinyl halides[14].

According to the latest findings[15] the alkenylphosphonium salts can be obtained in the reaction of α-silylylides with aromatic aldehydes. This synthetic pathway prompted us to disclosure our results in this field[16]. We have been interested in alkenylphosphonium salts as useful substrates for the synthesis of different β-substituted ylides to obtain functionalized allylic alcohols via Wittig reaction using various aliphatic aldehydes.

RESULTS AND DISCUSSION

It has been known that triphenyl[(trimethylsilyl)methylene]phosphorane reacts with α,β-unsaturated aldehydes via Peterson type elimination to give alkenylphosphonium salts[17] or with benzophenone to produce allenes[18]. We supposed that, when phosphorus atom in ylide becomes more electropositive due to the replacement of aryl substituents by alkyls, the Peterson type elimination would be more effective. We expected that in the reaction between tributyl[(trimethylsilyl)methylene]phosphorane and aldehydes, even the aliphatic ones, ethenylphosphonium salts should be formed exclusively in analogy to the work of McNulty[15].

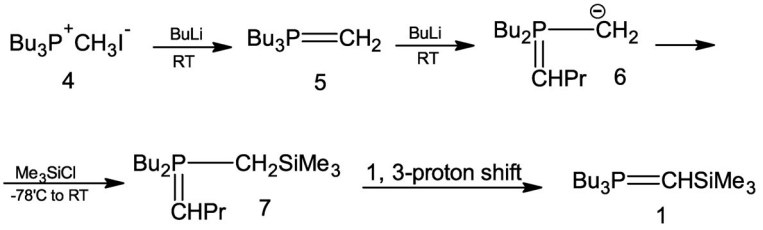
In this report we present our results on the reaction of tributyl[(trimethylsilyl)methylene]phosphorane (**1**) with numerous aliphatic aldehydes **2**, including acetaldehyde (**2a**), propionaldehyde (**2b**), lauraldehyde (**2c**), myristyl aldehyde (**2d**) and those containing different functionalities such as citral (**2e**), Garner aldehyde (**2f**) and myrtenal **2g** to produce the corresponding tributylalkenylphosphonium salts **3** (Scheme 1).



SCHEME 1
Synthesis of alkenylphosphonium salts **3** via reaction of tributyl[(trimethylsilyl)methylene]phosphorane (**1**) with aldehyde **2**

The synthesis of tributyl[(trimethylsilyl)methylene]phosphorane (**1**) is presented in Scheme 2. The phosphoryl anion **6** was prepared by the treatment of tributylmethylphosphonium iodide (**4**) with butyllithium at room temperature according to the known method[18] (Scheme 2).

Silylation of phosphoryl anion **6** with chlorotrimethylsilane at low temperature (–78 °C) afforded ylide **1** in good yield (Scheme 2). We suppose that silylation leads to intermediary ylide **7**, which undergoes transformation to the desired product **1** by 1,3-prototropic shift of methylene hydrogen connected to the silyl moiety to ylide carbon[19].



SCHEME 2
Synthesis of tributyl[(trimethylsilyl)methylene]phosphorane (**1**) from tributylmethylphosphonium iodide (**4**)

The syntheses of alkenylphosphonium salts were performed using filtered ("salt free") and unfiltered ethereal solutions of tributyl[(trimethylsilyl)methylene]phosphorane (**1**) to determine the influence of lithium salt on the reaction course.

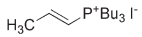
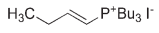
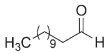
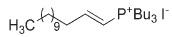
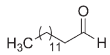
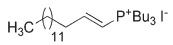
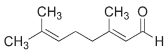
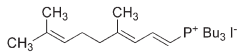
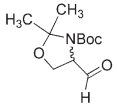
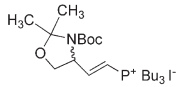
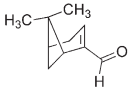
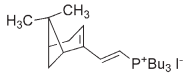
To obtain "salt free" solution of ylide **1**, we cooled ethereal solution to –78 °C and then allowed it to warm to room temperature. The solution was kept at this temperature for 20 min and then filtered under atmosphere of dry argon. Almost quantitative amount of lithium chloride and lithium iodide was filtered off (93–95%).

Ethereal solution of **1** was cooled to –78 °C and one equivalent of aldehyde was added. After 1 h the reaction mixture was allowed to warm to room temperature and 3 equivalents of NH_4I were added. The resulting mixture was kept at room temperature for 12 h. Addition of NH_4I to the reaction mixture let us obtain alkenylphosphonium salts as iodides. It was very important because *E* and *Z* stereoisomers of these iodides (not chlorides) could be separated using column chromatography on a silica gel.

The alkenylphosphonium salts **3** were isolated as iodides in 57–85% yields with moderate stereoselectivity favoring of the *Z*-alkene. *E*/*Z* ratio was determined by ^{1}H NMR and ^{31}P NMR spectroscopy of the crude reaction mixture (Table I).

Results presented in Table I also show that when the lithium salt has not been filtered off from the ylide solution (entries 3, 4 and 5), reaction with aldehydes gave almost the same amount of *E* and *Z* stereoisomers as compared with the reaction with "salt free" ylide solution. This indicates that

TABLE I
The alkenylphosphonium salts **3** obtained from the reaction of $Bu_3P{=}CHSiMe_3$ and aldehydes **2**

Entry	Aldehyde **2**	Alkenylphosphonium salt **3**	*E*/*Z*	Yield %	Molecular formula (M.w.)
1	**2a** 	**3a** 	1/2	65	$C_{15}H_{32}IP$ (370.30)
2	**2b** 	**3b** 	1/4	75	$C_{16}H_{34}IP$ (384.33)
3	**2c** 	**3c** 	1/5[a] 1.5.1[b]	72	$C_{25}H_{52}IP$ (510.57)
4	**2d** 	**3d** 	1/6[a] 1/6[b]	89	$C_{27}H_{56}IP$ (538.63)
5	**2e** 	**3e** 	1/1.4[a] 1/1.5[b]	77	$C_{23}H_{44}IP$ (478.48)
6	**2f** 	**3f** 	1/10	65	$C_{24}H_{47}INO_3P$ (555.52)
7	**2g** 	**3g** 	1/1.7	73	refs[15,16]

[a] The reaction has been performed with unfiltered ylide **1** solution. [b] Filtered ylide **1** solution was used.

small amount of lithium salts dissolved in ethereal solution (–70 °C) does not exert influence on the course of olefination reaction.

All compounds were identified on the basis of their analytical and spectroscopic data and the proposed structures are in agreement with the experimental data of similar compounds reported in the literature.

It is worth to note that the stereoselectivity observed in Peterson elimination offers interesting insight into the reaction mechanism. The stereoselectivity of the olefination of carbonyl compounds using silylated carbanions has been the subject of numerous debates and mechanistic considerations[20]. It was reported that preparation of α-alkyl-α,β-unsaturated esters from C-silylated enolates underwent stereoselectively, giving predominantly the *Z*-isomer. In contrast, simple α-silyl acetates were converted into the *E*-isomer predominatly. Until now, there is no generally accepted mechanism for the Peterson reaction.

It was postulated that in some cases, the formation of the O–Si bond and elimination of silanolate group are so rapid that there is at least 60° rotation about C–C bond[20b,20d,21,22]. So *Z*-stereoselectivity in that case, assuming irreversible addition of ylide at 109° to the carbonyl compounds, is the result of steric interaction of the carbonyl substituents with either the silyl or the phosphorane moiety during the first step of the reaction (steric approach control) (Fig. 1).

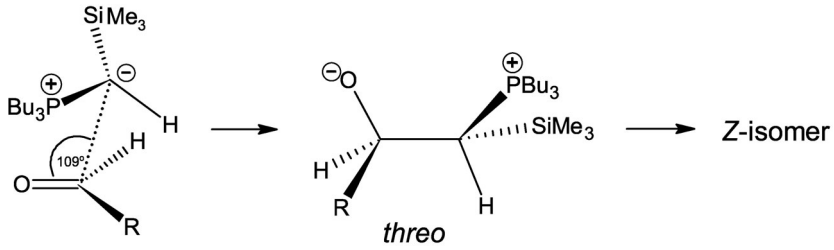
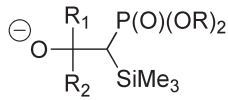


FIG. 1
Steric approach control favouring *Z*-alkenylphosphonium salts via the *threo*-betaine

We belive that this model explains formation of alkenylphosphonium salts.

Computational analysis on concerted and stepwise pathways for the simple model Wittig and Peterson olefination reaction revealed that intermediate like **8** (Fig. 2) which might form ethenylphosphonates by the loss of Me_3SiO^- or ethenylsilanes by the loss of $(RO)_2PO^-$ should eliminate only the silicon moiety[23].

If a close balance exists between silicon migration and phosphorus migration, when silicon substituents of **8** become more bulky (isopropyl instead of methyl), the stereoselective formation of a mixture of *trans*-ethenylsilane and *trans*-ethenylphosphonate is observed. This strongly indicate that there is no one common intermediate for these concurrent reactions[21b].



8

In the literature it was postulated that the steric approach control intermediate – betaine – may be formed not as the primary but as the secondary one[15]. It was assumed that it was the result of the formation of the respective oxaphosphetane intermediate as the primary product which may equilibrate with betaine.

However this explanation in examined reaction is very unlike because tributyl[(trimethylsilyl)methylene]phosphorane (**1**) belongs to stabilized ylides. This class forms oxaphosphetanes which are completely irreversible giving exclusively alkenes[24].

In conclusion, we have shown that [(trimethylsilyl)methylene]phosphoranes react cleanly with aliphatic aldehydes providing a general synthetic method for obtaining tributylalkenylphosphonium salts. We also present a very simple way for preparation of [(trimethylsilyl)methylene]-phosphoranes using cheap and easily available starting materials.

EXPERIMENTAL

All reactions were carried out under an argon atmosphere. The salts were obtained as viscous solids. All solvents were distilled and purified by standard procedures.

Tributylmethylphosphonium iodide (**4**) was prepared according to the previously described method[25,26]. IR spectra (ν, cm^{-1}) were recorded on a FT-IR Bruker ALPHA spectrometer with ATR platinum diamond reflection. ^1H (250 MHz), ^{13}C (62.89 or 176.07 MHz) and $^{31}P\{^1H\}$ NMR (101 MHz) spectra were recorded on Bruker DPX-250 and Bruker Avance II Plus 700 MHz spectrometers with TMS as an internal standard for ^1H and ^{13}C and 85% H_3PO_4 as external standard for ^{31}P NMR. ^{31}P NMR spectra were recorded using broad band proton decoupling. Chemical shifts (δ-scale) are reported in ppm, coupling constants (*J*) in Hz. All NMR spectra were recorded at room temperature. Elemental analyses were performed on a Perkin–Elmer PE 2400 analyzer. Chromatography isolations were performed using Merck silica gel 60 (40–270 mesh) for column chromatography and Merck plastic sheets, silica gel 60 F_{254}, for analytical TLC. Optical rotation ([α], g/dl) was measured in a 0.1 m cell (1 ml) on a Horiba high speed automatic polarimeter at 589 nm (sodium D line).

Lithium [Dibutyl(butylidene)phosphoranyl]methylide (**6**)

Into a flame-dried flask under argon was added dry diethyl ether (15 ml) and tributylmethylphosphonium iodide (**4**; 348 mg, 1.399 mmol). The mixture was stirred whereupon 1.6 M butyllithium solution (1.26 ml, 2.798 mmol) was added slowly at room temperature. The resulting mixture was kept at room temperature for 30 min and then spectroscopically analysed. ^{31}P NMR (101 MHz, diethyl ether, C_6D_6): 29.10. ^{1}H NMR (250 MHz, diethyl ether, C_6D_6): –0.96 d, 2 H, $^2J_{P\text{-}H}$ = 12.0 (PCH_2Li); –0.29 q, 1 H, $^2J_{P\text{-}H}$ = $^3J_{H\text{-}H}$ = 7.0 (P=CH), diagnostic signals only (other signals are overlaping by solvent).

Tributyl[(trimethylsilyl)methylene]phosphorane (**1**)

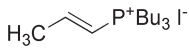
The ethereal solution containing **6** (312.4 mg, 1.399 mmol) was cooled to –78 °C and chlorotrimethylsilane (151 mg, 1.399 mmol) in diethyl ether (1 ml) was added dropwise. The resulting mixture was slowly warmed to room temperature and kept at this temperature for 30 min. ^{31}P NMR analyses of the solution shows that it contains only one organophosphorus compound, phosphorane **1**. ^{31}P NMR (101 MHz, diethyl ether, C_6D_6): 19.70. ^{1}H NMR (250 MHz, diethyl ether, C_6D_6): –1.1 d, 1 H, $^2J_{P\text{-}H}$ = 7.5 ($CHSiMe_3$), diagnostic signals only (other signals are overlaping by solvent).

Synthesis of Alkenylphosphonium Salts **3**. General procedure

The ethereal solution (15 ml) of tributyl[(trimethylsilyl)methylene]phosphorane (**1**; 403 mg, 1.399 mmol) was cooled to –78 °C and the aldehyde **2** (1.399 mmol in 2 ml Et_2O) was slowly added via syringe at that temperature. The mixture was allowed to warm to room temperature and ammonium iodide (608 mg, 4.197 mmol) was added. The resulting mixture was stirred for 12 h. After that time the mixture was concentrated to remove diethyl ether and to the residue chloroform (10 ml) was added. The mixture was filtered and concentrated to give crude alkenylphosphonium salts **3** (*E* and *Z* mixture, Table I).

Analytically pure sample of *E* and *Z* stereoisomers has been obtained after purification, which was accomplished by silica gel chromatography, eluting with ethyl acetate.

Tributylprop-1-enylphosphonium Iodide (**3a**)



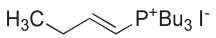
Crude product 293 mg (65%), *E* and *Z* mixture. *E*/*Z* = 1/2.

E-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 25.67. ^{1}H NMR (250 MHz, $CDCl_3$): 0.98 t, 9 H, $^3J_{H\text{-}H}$ = 7.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.43–1.87 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 2.10 d, 3 H, $^3J_{H\text{-}H}$ = 4.5 (CH=CH-CH_3); 2.28–2.46 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 6.15 m, 1 H, $^2J_{P\text{-}H}$ = 21.0, $^3J_{H\text{-}H}$ = 15.7, $^4J_{H\text{-}H}$ = 1.7 (Bu_3P^+CH=CH); 7.00 m, 1 H, $^3J_{P\text{-}H}$ = 19.7, $^3J_{H\text{-}H}$ = 15.7, $^3J_{H\text{-}H}$ = 7.5 (Bu_3P^+CH=C**H**-CH_3). ^{13}C NMR with broad band decoupling (62.89 MHz, $CDCl_3$): 14.0; 17.8; 20.1 d, $^1J_{C\text{-}P}$ = 51.0; 23.8; 24.0 d, $^2J_{C\text{-}P}$ = 17.6; 105.2 d, $^1J_{C\text{-}P}$ = 78.7; 134.1 d, $^2J_{C\text{-}P}$ = 17.0.

Z-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 23.68. ^{1}H NMR (250 MHz, $CDCl_3$): 0.95 t, 9 H, $^3J_{H\text{-}H}$ = 7.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.30–1.85 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 2.04 d, 3 H, $^3J_{H\text{-}H}$ = 4.5 (CH=CH-CH_3); 2.15–2.36 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 5.93 m, 1 H, $^2J_{P\text{-}H}$ = 19.7, $^3J_{H\text{-}H}$ = 12.7, $^4J_{H\text{-}H}$ = 1.5 (C**H**=CH-CH_3); 7.09 m, 1 H, $^2J_{P\text{-}H}$ = 37.2, $^3J_{H\text{-}H}$ = 12.7, $^3J_{H\text{-}H}$ = 7.5 (CH=C**H**-CH_3). ^{13}C NMR with broad band decoupling (62.89 MHz, $CDCl_3$): 13.8; 17.5; 20.8

d, $^1J_{C\text{-}P}$ = 47.5; 23.9; 24.1 d, $^2J_{C\text{-}P}$ = 15.8; 108.7 d, $^1J_{C\text{-}P}$ = 81.0; 136.0 d, $^2J_{C\text{-}P}$ = 8.7). IR: 1618 (CH=CH). For $C_{15}H_{32}IP$ (370.30) calculated: 48.65% C, 8.71% H; found: 48.44% C, 8.59% H.

But-1-enyltributylphosphonium Iodide (**3b**)

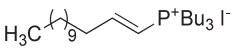


Crude product 403 mg (75%), *E* and *Z* mixture. *E*/*Z* = 1/4.

E-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 25.70. ^{1}H NMR (250 MHz, $CDCl_3$): 0.92 t, 3 H, $^3J_{H\text{-}H}$ = 7.5 (CH=CHCH$_2$C**H**$_3$); 0.95 t, 9 H, $^3J_{H\text{-}H}$ = 6.5 (C**H**$_3$CH$_2$CH$_2$CH$_2$)$_3$P); 1.23 qwi, 2 H, $^3J_{H\text{-}H}$ = 7.0 (CH=CHC**H**$_2$CH$_3$); 1.46–1.71 m, 12 H ((CH$_3$C**H**$_2$C**H**$_2$CH$_2$)$_3$P); 2.31–2.49 m, 6 H ((CH$_3$CH$_2$CH$_2$C**H**$_2$)$_3$P); 6.13 dd, 1 H, $^2J_{P\text{-}H}$ = 19.7, $^3J_{H\text{-}H}$ = 17.7 (Bu$_3$P$^+$C**H**=CH); 7.05 m, 1 H, $^3J_{P\text{-}H}$ = 43.2, $^3J_{H\text{-}H}$ = 17.7, $^3J_{H\text{-}H}$ = 7.5 (Bu$_3$P$^+$CH=C**H**). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 12.8; 13.7; 21.7 d, $^1J_{C\text{-}P}$ = 49.2; 23.7; 23.8 d, $^2J_{C\text{-}P}$ = 19.3; 26.7; 107.1 d, $^1J_{C\text{-}P}$ = 77.4; 136.1 d, $^2J_{C\text{-}P}$ = 18.2.

Z-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 23.50. ^{1}H NMR (250 MHz, $CDCl_3$): 0.88 t, 3 H, $^3J_{H\text{-}H}$ = 7.5 (CH=CHCH$_2$C**H**$_3$); 0.91 t, 9 H, $^3J_{H\text{-}H}$ = 6.5 ((C**H**$_3$CH$_2$CH$_2$CH$_2$)$_3$P); 1.19 qwi, 2 H, $^3J_{H\text{-}H}$ = 7.0 (CH=CHC**H**$_2$CH$_3$); 1.40–1.70 m, 12 H ((CH$_3$C**H**$_2$C**H**$_2$CH$_2$)$_3$P); 2.25–2.47 m, 6 H ((CH$_3$CH$_2$CH$_2$C**H**$_2$)$_3$P); 5.83 dd, 1 H, $^2J_{P\text{-}H}$ = 19.7, $^3J_{H\text{-}H}$ = 12.7 (Bu$_3$P$^+$C**H**=CH); 6.90 m, 1 H, $^3J_{P\text{-}H}$ = 43.2, $^3J_{H\text{-}H}$ = 12.7, $^3J_{H\text{-}H}$ = 7.7 (Bu$_3$P$^+$CH=C**H**). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 12.0; 13.3; 20.3 d, $^1J_{C\text{-}P}$ = 48.9; 23.4; 23.5 d, $^2J_{C\text{-}P}$ = 15.5; 26.3; 107.0 d, $^1J_{C\text{-}P}$ = 79.9; 136.0 d, $^2J_{C\text{-}P}$ = 7.0. IR: 1618 (CH=CH). For $C_{16}H_{34}IP$ (384.33) calculated: 50.00% C, 8.92% H; found: 49.83% C, 8.68% H.

Tributyltridec-1-enylphosphonium Iodide (**3c**)

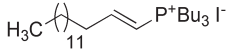


Crude product 515 mg (72 %), *E* and *Z* mixture. *E*/*Z* = 1/5[a], *E*/*Z* = 1/5.1[b] (see Table I).

E-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 25.59. ^{1}H NMR (250 MHz, $CDCl_3$): 0.86 t, 3 H, $^3J_{H\text{-}H}$ = 7.5 ((CH$_2$)$_9$C**H**$_3$); 0.98 t, 9 H, $^3J_{H\text{-}H}$ = 6.5 ((C**H**$_3$CH$_2$CH$_2$CH$_2$)$_3$P); 1.10–1.40 m, 18 H ((C**H**$_2$)$_9$CH$_3$); 1.45–1.76 m, 12 H ((CH$_3$C**H**$_2$C**H**$_2$CH$_2$)$_3$P); 2.23–2.39 m, 2 H (CH=CH-C**H**$_2$); 2.44–2.69 m, 6 H ((CH$_3$CH$_2$CH$_2$C**H**$_2$)$_3$P); 6.25 m, 1 H, $^2J_{P\text{-}H}$ = 20.7, $^3J_{H\text{-}H}$ = 17.5, $^4J_{H\text{-}H}$ = 1.6 (Bu$_3$P$^+$C**H**=CH); 7.10 m, 1 H, $^3J_{P\text{-}H}$ = 19.8, $^3J_{H\text{-}H}$ = 17.5, $^3J_{H\text{-}H}$ = 7.5 (Bu$_3$P$^+$CH=C**H**). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 14.2; 14.9; 20.5; 21.0 d, $^1J_{C\text{-}P}$ = 48.9; 22.7; 23.1; 23.7 d, $^2J_{C\text{-}P}$ = 17.7; 29.1; 32.3; 42.0; 98.7 d, $^1J_{C\text{-}P}$ = 82.9; 136.2 d, $^2J_{C\text{-}P}$ = 19.0.

Z-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 23.45. ^{1}H NMR (250 MHz, $CDCl_3$): 0.83 t, 3 H, $^3J_{H\text{-}H}$ = 7.5 ((CH$_2$)$_9$C**H**$_3$); 0.95 t, 9 H, $^3J_{H\text{-}H}$ = 6.5 ((C**H**$_3$CH$_2$CH$_2$CH$_2$)$_3$P); 1.05–1.33 m, 18 H ((C**H**$_2$)$_9$CH$_3$); 1.40–1.72 m, 12 H ((CH$_3$C**H**$_2$C**H**$_2$CH$_2$)$_3$P); 2.13–2.36 m, 2 H (CH=CH-C**H**$_2$); 2.40–2.66 m, 6 H ((CH$_3$CH$_2$CH$_2$C**H**$_2$)$_3$P); 6.10 m, 1 H, $^2J_{P\text{-}H}$ = 19.7, $^3J_{H\text{-}H}$ = 12.7, $^4J_{H\text{-}H}$ = 1.7 (Bu$_3$P$^+$C**H**=CH); 7.05 m, 1 H, $^3J_{P\text{-}H}$ = 43.2, $^3J_{H\text{-}H}$ = 12.7, $^3J_{H\text{-}H}$ = 7.7 (Bu$_3$P$^+$CH=C**H**). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 13.9; 14.8; 20.8; 21.6 d, $^1J_{C\text{-}P}$ = 49.9; 23.0; 23.4; 23.9 d, $^2J_{C\text{-}P}$ = 15.5; 29.7; 32.6; 41.6; 98.0 d, $^1J_{C\text{-}P}$ = 83.9; 134.7 d, $^2J_{C\text{-}P}$ = 7.0. IR: 1618 (CH=CH). For $C_{25}H_{52}IP$ (510.57) calculated: 58.81% C, 4.93% H; found: 58.59% C, 4.80% H.

Tributylpentadec-1-enylphosphonium Iodide (**3d**)

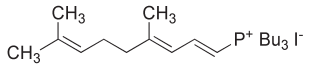


Crude product 677 mg (89%), *E* and *Z* mixture. *E*/*Z* = 1/6.

E-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 25.56. ^{1}H NMR (250 MHz, $CDCl_3$): 0.90 t, 3 H, $^3J_{H-H}$ = 7.5 ($(CH_2)_{11}CH_3$); 1.08 t, 9 H, $^3J_{H-H}$ = 6.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.17–1.42 m, 22 H ($(CH_2)_{11}CH_3$); 1.46–1.78 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 2.27–2.45 m, 2 H (CH=CH-CH_2); 2.48–2.81 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 6.13 m, 1 H, $^2J_{P-H}$ = 20.7, $^3J_{H-H}$ = 17.5, $^4J_{H-H}$ = 1.7 (Bu_3P^+CH=CH); 6.62 m, 1 H, $^3J_{P-H}$ = 20.2, $^3J_{H-H}$ = 17.5, $^3J_{H-H}$ = 7.0 (Bu_3P^+CH=CH). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 13.9; 14.6; 20.2; 20.5 d, $^1J_{C-P}$ = 48.0; 23.0; 24.2; 24.4 d, $^2J_{C-P}$ = 18.0; 28.5; 33.1; 42.7; 99.1 d, $^1J_{C-P}$ = 82.0; 137.0 d, $^2J_{C-P}$ = 20.0.

Z-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 23.51. ^{1}H NMR (250 MHz, $CDCl_3$): 0.85 t, 3 H, $^3J_{H-H}$ = 7.5 ($(CH_2)_{11}CH_3$); 0.98 t, 9 H, $^3J_{H-H}$ = 6.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.10–1.40 m, 22 H ($(CH_2)_{11}CH_3$); 1.40–1.75 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 2.20–2.40 m, 2 H (CH=CH-CH_2); 2.40–2.70 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 5.88 m, 1 H, $^2J_{P-H}$ = 19.7, $^3J_{H-H}$ = 12.7, $^4J_{H-H}$ = 1.7 (Bu_3P^+CH=CH); 6.94 m, 1 H, $^3J_{P-H}$ = 43.2, $^3J_{H-H}$ = 12.7, $^3J_{H-H}$ = 7.0 (Bu_3P^+CH=CH). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 13.5; 14.2; 20.0; 20.9 d, $^1J_{C-P}$ = 49.4; 23.0; 23.7; 24.0 d, $^2J_{C-P}$ = 15.5; 29.6; 32.3; 41.4; 98.9 d, $^1J_{C-P}$ = 82.7; 135.5 d, $^2J_{C-P}$ = 7.7. IR: 1616 (CH=CH). For $C_{27}H_{56}IP$ (538.63) calculated: 60.21% C, 10.48% H; found: 59.87% C, 10.29% H.

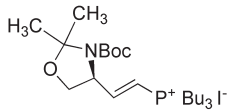
Tributyl(4,8-dimethylnona-1,3,7-trienyl)phosphonium Iodide (**3e**)



Crude product 516 mg (77%), *E*/*Z* mixture on both stereogenic centres. 1*E*/1*Z* = 1/4[a], 1*E*/1*Z* = 1/5[b] (see Table I).

^{31}P NMR (101 MHz, $CDCl_3$): 23.14 (main stereoisomer); 23.26, 26.43, 26.55. ^{1}H NMR (250 MHz, $CDCl_3$): main stereoisomer: (1*Z*,3*E*)-tributyl(4,8-dimethylnona-1,3,7-trienyl)phosphonium iodide (diagnostic vinyl signals because of strong overlaping with other signals): 5.66 dd, 1 H, $^2J_{P-H}$ = 17.7, $^3J_{H-H}$ = 12.7 (Bu_3P^+CH=CH); 7.54 dt, 1 H, $^3J_{P-H}$ = 53.5, $^3J_{H-H}$ = 12.7 (Bu_3P^+CH=CH). ^{13}C NMR with broad band decoupling (62.89 MHz, $CDCl_3$): (diagnostic vinyl signals because of strong overlapping with other signals): *1E-isomer*: 104.6 d, $^1J_{C-P}$ = 81.9; 129.3 d, $^2J_{C-P}$ = 20.7. *1Z-isomer*: 101.8 d, $^1J_{C-P}$ = 75.1; 123.2 d, $^2J_{C-P}$ = 8.7. IR: 1627 (CH=CH). For $C_{23}H_{44}IP$ (478.48) calculated: 57.73% C, 9.27% H; found: 57.50% C, 9.11% H.

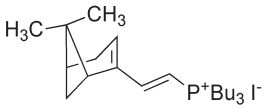
(*S*)-{2-[3-(*tert*-Butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl]ethenyl}-tributylphosphonium Iodide (**3f**)



Crude product 506 mg (65%), *E* and *Z* mixture. *E*/*Z* = 1/10.

Z-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 25.97. ^{1}H NMR: (250 MHz, $CDCl_3$): 0.98 t, 9 H, $^3J_{H-H}$ = 6.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.50–1.78 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 1.52 s, 9 H (($CH_3)_3C(O)OC$-); 1.56 s, 3 H (-$C(CH_3)CH_3$); 1.58 s, 3 H (-$C(CH_3)CH_3$); 2.56–2.70 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 3.70–4.01 m, 1 H (-CH-CH_2-O-); 4.25–4.60 m, 1 H (-CH-CH_2-O-); 4.50–4.75 m, 1 H (-CH-N-); 6.20 dd, 1 H, $^2J_{P-H}$ = 17.1, $^3J_{H-H}$ = 13.5 (P^+CH=CH); 6.72 m, 1 H, $^3J_{P-H}$ = 42.9, $^3J_{H-H}$ = 13.5, $^3J_{H-H}$ = 11 (P^+CH=CH). ^{13}C NMR with broad band decoupling (62.89 MHz, $CDCl_3$): 12.9; 19.9 d, $^1J_{C-P}$ = 48.9; 23.0; 23.5 d, $^2J_{C-P}$ = 15.1; 26.3; 27.3; 27.6; 28.1; 58.4; 58.0; 62.9; 80.8; 81.5; 93.1; 93.4; 109.1 d, $^1J_{C-P}$ = 74.3; 140.2 d, $^2J_{C-P}$ = 13.1; 151.3; 152.9. IR: 1627 (CH=CH). For $C_{24}H_{47}IP$ (555.52) calculated: 51.89% C, 8.53% H; found: 51.61% C, 8.36% H.

Tributyl[2-(6,6-dimethylbicyclo[3.1.1.]hept-2-en-2-yl)ethenyl]phosphonium Iodide (**3g**)



Crude product 487 mg (73%), *E* and *Z* mixture. *E*/*Z* = 1/1.7.

E-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 27.40. ^{1}H NMR: (250 MHz, $CDCl_3$): 0.77 s, 3 H ($C(CH_3)_2$); 0.98 t, 9 H, $^3J_{H-H}$ = 6.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.20 d, 2 H, $^3J_{H-H}$ = 7.2 (CHCH_2CH); 1.39 s, 3 H ($C(CH_3)_2$); 1.54–1.70 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 1.95–2.20 m, 1 H (CH=C-CH); 2.14 t, 2 H, $^3J_{H-H}$ = 6.8 (C=CHCH_2CH); 2.35–2.54 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 2.35–2.54 m, 1 H ($CH_2CHC(CH_3)_2$); 5.74 t, 1 H, $^2J_{P-H}$ = 19.7, $^3J_{H-H}$ = 18.2 (P^+CH=CH); 6.37 s, 1 H (P^+CH=CHC=CH); 7.27 dd, 1 H, $^3J_{P-H}$ = 36.5, $^3J_{H-H}$ = 18.2 (P^+CH=CH). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 13.8; 20.3 d, $^1J_{C-P}$ = 48.8; 20.7; 23.3; 23.8 d, $^2J_{C-P}$ = 17.6; 26.2; 29.9; 31.6; 38.2; 40.6; 42.8; 98.8 d, $^1J_{C-P}$ = 83.3; 138.8; 146.2 d, $^2J_{C-P}$ =18.2; 153.6.

Z-isomer: ^{31}P NMR (101 MHz, $CDCl_3$): 23.10. ^{1}H NMR (250 MHz, $CDCl_3$): 0.90 s, 3 H ($C(CH_3)_2$); 0.99 t, 9 H, $^3J_{H-H}$ = 6.2 (($CH_3CH_2CH_2CH_2)_3P$); 1.24 d, 2 H, $^3J_{H-H}$ = 7.2 (CHCH_2CH); 1.41 s, 3 H ($C(CH_3)_2$); 1.55–1.66 m, 12 H (($CH_3CH_2CH_2CH_2)_3P$); 2.10–2.20 m, 1 H (CH=C-CH); 2.30 t, 1 H, $^3J_{H-H}$ = 6.8 (CH=C-CH); 2.52–2.66 m, 6 H (($CH_3CH_2CH_2CH_2)_3P$); 2.52–2.66 m, 1 H ($CH_2CHC(CH_3)_2$); 5.75 dd, 1 H, $^2J_{P-H}$ = 16.5, $^3J_{H-H}$ = 13.5 (P^+CH=CH); 6.01 s, 1 H (P^+CH=CHC=CH); 7.26 dd, 1 H, $^3J_{P-H}$ = 42.5, $^3J_{H-H}$ = 13.5 (P^+CH=CH). ^{13}C NMR with broad band decoupling (176.07 MHz, $CDCl_3$): 13.8; 20.2 d, $^1J_{C-P}$ = 49.3; 20.3; 23.6; 24.0 d, $^2J_{C-P}$ = 15.6; 26.0; 29.9; 31.1; 38.4; 40.8; 44.9; 99.3 d, $^1J_{C-P}$ = 82.7; 139.1; 146.2 d, $^2J_{C-P}$ = 7.0; 153.4. IR: 1616–1595 (broad band), (CH=CH). Optical rotation: [α] –58.05 (*c* = 0.75, $CHCl_3$). For $C_{23}H_{42}IP$ (476.47) calculated: 57.98% C, 8.89% H; found: 57.72% C, 8.70% H.

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