Reactivity and Utility of Allenylphosphonates: Formation of a Novel Hydroperoxide and Propargylic Alcohol and Facile Thiol Addition under Catalyst-Free, Solvent-Free Conditions

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Abstract: 2-(Propa-1,2-dienyl)-, 2-(buta-1,2-dienyl)-, and 2-(3-methylbuta-1,2-dienyl)-substituted 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxides 1a–c react readily upon heating with thiols under catalyst-free, base-free, and solvent-free conditions to give sulfanyl-substituted phosphonates. The reaction undergoes to essential completion within 15 minutes under microwave radiation. While 1a,b react with 4-chlorothiophenol to afford both 2-[2-(4-chlorophenylsulfonyl)prop-1-enyl]-12 and 2-[2-(4-chlorophenylsulfanyl)prop-2-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxides 13, 1c gives 2-[2-(4-chlorophenylsulfonyl)-3-methylbut-2-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (13d) regioselectively. Molecular oxygen undergoes a novel reaction with the allene 1c to give propargylic alcohol 2-(3-hydroxy-3-methylbut-1-ynyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (16) via the corresponding hydroperoxide; the structures of these were confirmed by X-ray crystallography. The synthetic utility of the sulfanyl-substituted allylphosphonate 13d in the Horner–Wadsworth–Emmons reaction to afford synthetically valuable sulfanyl-substituted buta-1,3-dienes and a conjugated triene is demonstrated.

Key words: allenes, thiol addition, oxygenation, Horner–Wadsworth–Emmons reaction, allenylphosphonates

Allenes or 1,2-dienes are potential precursors for a variety of molecules of industrial and pharmaceutical importance.1,2 Among these, allenylphosphonates (phosphorylated allenes) 1a–c constitute a readily accessible family of allenes that can be used as versatile building blocks in organic synthesis.3 Since in substituted allenes, phosphorus can impart a different electronic constraint relative to a carbon or hydrogen on the intermediates, the sterechemistry of the products in the reactions using allenylphosphonates and phenyl-substituted allenes may be the result of different pathways. In addition, the experimental conditions also could influence the final outcome of the reaction. As an example, in the simple addition reaction of allene 2 with a nucleophile shown in Scheme 1, the incoming nucleophile can, in principle, attack any of the three carbon centers, α, β, or γ depending upon the substituents present and the conditions used. Although the resulting primary products 3–6 are all allenes, geometrical isomerism is also possible.

The simple reactions of allenes are those with nucleophiles like amines, alcohols, phenols, or thiols leading to vinyl and/or allylphosphonates of types 4 or 5 where attack takes place at the β-carbon.4,5 The reactions with amines can be extended to those with nucleobases as well as gaseous ammonia and in our previous work we have shown that the precursor 7 gives both trans-vinyl and allyl products 8–10, but in the case of ammonia, cis-vinylphosphonate 11 is preferentially formed (Scheme 2).5 Attack at the γ-carbon (umpolung addition) takes place with phenols for the phosphine-catalyzed reactions.6 The addition of thiols to allenes is a well-known protocol for the preparation of vinyl and allylic sulfides; these reactions were conducted using UV radiation or palladium catalysis.7 Earlier, reactions of thiols with phosphorylated allenes were performed in the presence of a base (e.g., NaOEt) and a solvent (e.g., EtOH).3a,8

Scheme 1

By keeping the above reactions in mind and in continuation of our investigations on organophosphorus chemistry,3,5,7 we report herein the direct addition of thiols with the inexpensive phosphorylated allenes 1a–c under environmentally benign, catalyst-free, and solvent-free conditions. While doing so, we have observed a novel reaction of 1c with dioxygen in which the first formed hydroperoxide leads to a phosphono-propargylic alcohol, as shown by X-ray crystallography. We also report the successful utilization of the sulfanyl-substituted allylphosphonate products to afford synthetically useful 3-sulfanyl-substiti-
tuted trans-buta-1,3-dienes via Horner–Wadsworth–Emmons (HWE) reaction.

The various vinyl 12a–c and allyl products 13a,b,d,e isolated from the reaction of 1a–c with thiols are shown in Scheme 3 and Table 1. Treatment of 1a with 4-chlorothiophenol without solvent at 100 °C for 4–6 hours afforded an isomeric mixture of 12a and 13a (combined yield 80%) in ~2:3 ratio by 31P NMR, thus showing that a catalyst or base is unnecessary for this reaction. It should be noted that in the final reaction mixture, only one vinylphosphonate isomer is present for which we assign E-stereochemistry (tentative). We also performed the same reaction using palladium(II) acetate in tetrahydrofuran, but the product ratio remained unchanged; under microwave conditions also the essentially the same ratio was maintained but the reaction was essentially complete in 15 minutes. The product distribution, however, is distinctly different from that of the palladium(II) acetate catalyzed addition of benzenethiol in tetrahydrofuran to phenylallene (wherein a mixture of three isomers was obtained) or tert-butyl- or cyclohexylallene (RCH=C=CH2 where R = t-Bu, Cy) in which the products RCH2C(SPh)=CH2 are formed regioselectively.7b

We have checked the 31P NMR spectrum of the reaction mixture after heating 1a with 4-chlorothiophenol at 70–80 °C for 15 minutes without solvent (or with CHCl3, 6 h) and found that the allyl product 13a [δ(P) 20.5] is not formed. The mixture contains only the vinyl product 12a [δ(P) 12.9], precursor 1a [δ(P) 8.8], and an unknown species [δ(P) 13.9] (Figure 1).10 At present we cannot assign a structure to the intermediate, but based on 31P NMR it appears to contain the (5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)methylene group [(OCH2CMe2CH2O)P(O)CH=]. It is possible that the peak at δ(P) 13.9 is due to the β-ketophosphonate 5,5-dimethyl-2-(2-oxopropyl)-1,3,2-dioxaphosphinan 2-oxide [(OCH2CMe2CH2O)P(O)CH2COCH3], but a pure sample of this compound did not react with 4-chlorothiophenol upon heating at 100 °C for 48 hours.

The ratio of the vinyl to allyl phosphonates 12/13 depends on the substituents present on the allene as well as on the thiol. In the case of 1b, a regioisomeric mixture (12b and 13b) was obtained in 1:2 ratio (by 31P NMR spectrum of the reaction mixture) and for 1c, a regioselective product 13d was obtained in 80% yield. We used mainly 4-chlorothiophenol as it is a solid and gives less stench compared to other thiols. While treatment of 1a with

### Table 1 Formation of 12 and 13

<table>
<thead>
<tr>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>Product</th>
<th>Yield (%)</th>
<th>δ(P) NMR, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>4-ClC6H4</td>
<td>12a</td>
<td>34</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13a</td>
<td>45</td>
<td>20.5</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>4-ClC6H4</td>
<td>12b</td>
<td>23</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13b</td>
<td>41b</td>
<td>21.5, 21.9 (ratio 9:1)</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>Cy</td>
<td>12c</td>
<td>20</td>
<td>13.7</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>4-ClC6H4</td>
<td>13d</td>
<td>80</td>
<td>22.3</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>CH2CH2OH</td>
<td>13e</td>
<td>70</td>
<td>23.9</td>
</tr>
</tbody>
</table>

*a* Isolated yield.

*b* E/Z Isomeric mixture.

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cyclohexanethiol gave a mixture of three phosphonates [δ(P) 12.0, 13.1, 14.8] from which 12c [δ(P) 12.0] was isolated in 20% yield, that with 2-sulfanylethanol afforded the allyl product 13e [δ(P) 23.9; isolated yield 70%] stereoselectively.

What is perhaps more interesting in terms of reactivity is that when we used an old sample of 1c in reaction with 4-chlorothiophenol, we isolated the unexpected product 14 reproducibly in about 10% yield. This compound showed an IR band at 3380 cm⁻¹ and hence an X-ray crystal structure (Figure 2) was determined. As is evident, the hydroxy group could not have entered from either of the expected precursors, and hence we examined the original sample. This sample had some viscous liquid present along with solid and the 31P NMR spectrum showed peaks at δ –12.2 and –11.4 (1:5) in addition to that expected for 1c (δ 9.9). Careful chromatography [Rf ~0.58 for both (EtOAc–hexane, 1:1)] followed by crystallization afforded the compounds 15 and 16 (Scheme 4).¹¹ We then found that exposure of 1c to air for ~30 days leads to its conversion into 16 (50%) along with a small quantity of 15 (ca. 5%). Both of these compounds were characterized by single-crystal X-ray crystallography (Figure 3). It is likely that compound 14 is formed by the cis addition of 4-chlorothiophenol to 16.

5,5-Diethyl-2-(3-methylbuta-1,2-dienyl)-1,3,2-dioxaphosphinane 2-oxide (δP 10.9) also reacts with molecular oxygen and the propargylic alcohol 17 could be isolated readily (Figure 4).¹² This result shows that reaction of allenylphosphonates containing terminal =CMe₂ groups with molecular oxygen is general.

Compound 16 is less reactive towards 4-chlorothiophenol compared to 1c. A better route to 16 is to expose 1c to air for ~30 days and then use chromatography to separate 16 (ca. 50% yield). Although slow oxidation (autoxidation) is common for many unsaturated compounds in light/air over a long period,¹³ and compound 1c has been known in the literature for a long time, there has been no report on its stability when exposed to air. We could distill it at 180 °C/9 mbar and could keep it under water for 48 hours with
<5% decomposition (to 15 and 16). Upon treatment with hydrogen peroxide, 1c gave a mixture with 15 and 16 as the major products (~50%).

It may be noted that the sulfanyl-substituted allylphosphonates 13a,b,d,e have a PCH$_2$ group from which deprotonation can easily be effected and utilized in HWE reaction with aldehydes to afford buta-1,3-diienes. In the present work we have utilized the easily synthesized 13d as the precursor for the HWE reaction (Scheme 5). Reactions with aldehydes were performed in the presence of the inexpensive base sodium hydride at room temperature for 6–10 hours using tetrahydrofuran as solvent. The trans-buta-1,3-diienes 18, conjugated trans-triene 19, and the bis(trans-buta-1,3-diene) 20 were isolated in good yields; refluxing temperature was required in the synthesis of 20. The stereochemistry of these dienes is confirmed by checking the single-crystal X-ray crystal structure for 18a (Figure 5). It should be noted that earlier 2-(phenylsulfonyl)-substituted 1,3-diienes were prepared by Zhijie and Padwa using tetrakis(triphenylphosphine)palladium(0)-catalyzed cross-coupling of α-allenyl acetates CH$_2$:CH=C(SPh)CR$_1$R$_2$(OAc) with several terminal alkyynes. These sulfur containing buta-1,3-diienes hold potential for the synthesis of new cyclic ring systems. However, in their case a cis-butadiene structure was proposed while our route gives trans-buta-1,3-diienes as shown by the X-ray crystal structure of 18a.

Figure 5 An ORTEP drawing of 18a.

The synthetic potential of the thiol addition reaction presented here is further illustrated in the case of benzamido heterocyclic phosphonate 13f (Figure 6). We also have obtained the nucleobase appended phosphonate 13g [$^1$H and $^{31}$P NMR], but the sample could be obtained only in ~90% purity.

In summary, we have synthesized the sulfanyl-substituted allylphosphonates by the direct addition of thiols with phosphorylated allenes under nonbasic, catalyst-free, and solvent-free conditions. The reactions are complete within

Scheme 5

Figure 6

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15 minutes under microwave irradiation. Molecular oxygen undergoes a novel reaction with the allenes 1c (and its 5,5-diethyl analogue), to lead to the propargylic alcohols 16 via the hydroperoxide 15; the structures of these were confirmed by X-ray crystallography. Utilization of sulfanyl-substituted allylphosphonates in the HWE reaction to afford synthetically valuable sulfanyl-substituted buta-1,3-diienes and a conjugated triene is demonstrated.

Chemicals were purified when required according to standard procedures. All reactions, unless stated otherwise, were performed in a dry N2 atmosphere. 1H, 13C and 31P{H} NMR spectra were recorded using a 200 MHz or a 400 MHz spectrometer in CDCl3 (unless stated otherwise) with shifts referenced to TMS (δ = 0) or 85% H3PO4 (δ = 0). IR spectra were recorded on an FT/IR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a CHNS analyzer. Mass spectra were recorded using a GCMS-QP2010 and LCMS 2010A.

Precurors 5,5-dimethyl-2-(propa-1,2-dienyl)-1,3,2-dioxaphosphinane 2-oxide 1a, 2-(buta-1,2-dienyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide 1b, and 5,5-dimethyl-2-(methylbuta-1,2-dienyl)-1,3,2-dioxaphosphinane 2-oxide 1c were prepared using literature procedures. 5,5-Diethyl-2-(methylbuta-1,2-dienyl)-1,3,2-dioxaphosphinane 2-oxide was prepared in a manner similar to 1c as a liquid; 1H NMR: δ = 0.90–1.00 (m, 1.76 (brm), 3.92–4.19 (m), 5.16 (m); 31P NMR: δ = 10.9.

2-[2-(4-Chlorophenylsulfanyl)prop-1-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (12a); Typical Procedure
A mixture of 1a (0.30 g, 1.6 mmol) and 4-chlorophenol (0.28 g, 1.9 mmol) was heated neat at 90–100 °C in a 10-mL round bottomed flask for 4–6 h. The products formed were separated by column chromatography (silica gel, EtOAc–hexane, 2:3) to give initially 12a and then 13a.

2-[2-(4-Chlorophenylsulfanyl)prop-1-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (12a) Derivative 12b Yield: 0.12 g (23%); mp 90–92 °C.
IR (KBr): 1588, 1474, 1373, 1240, 1059, 1011 cm⁻¹.
1H NMR (400 MHz, CDCl3): δ = 0.90, 1.04 (2 s, 6 H, 2 CH3), 1.30 (t, J = 7.2 Hz, 3 H, CH3CH2), 2.81 (q, J = 7.2 Hz, 2 H, CH2CH3), 3.70 (dd [app t], J = 11.2, 11.2 Hz, 2 H, OCH3), 4.11 [dd (app t), J = 11.2, 11.2 Hz, 2 H, OCH3], 4.88 (d, J = 14.3 Hz, 1 H, =CH), 7.44 (br, 4 H, Ar-H).
13C NMR (50 MHz, CDCl3): δ = 14.6 (s, CH3CH2), 21.5 (s, 2 CH3, merged together), 28.4 (d, J = 6.1 Hz, CH2CH3), 32.5 (d, J = 5.0 Hz, CMe2), 75.3 (d, J = 6.1 Hz, OCH3), 101.7 (d, J = 190.4 Hz, PCH), 128.2, 130.1, 136.5, 137.0, 169.8 (d, J = 13.3 Hz, =CH2CH3).
31P NMR (160 MHz, CDCl3): δ = 12.9 (s).

2-[2-(4-Chlorophenylsulfanyl)but-1-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (13b)
Following the procedure for 12a/13a using allene 1b (0.30 g, 1.5 mmol) and the thiol, these compounds were synthesized.

2-[2-(4-Chlorophenylsulfanyl)prop-1-enyl]-1,3,2-dioxaphosphinane 2-Oxide (13c)

Yield: 0.21 g (41%); mp 78–80 °C.
IR (KBr): 1476, 1267, 1092, 1055, 1005 cm⁻¹.
1H NMR (400 MHz, CDCl3): δ = 1.02, 1.08 (2 s, 6 H, 2 CH3), 1.84–1.85 (m, 3 H, =CCH2), 2.87 (d, J = 21.2 Hz, 2 H, PCH2), 3.81–4.21 (m, 4 H, OCH3), 6.17–6.20 (m, 1 H, =CH), 7.24–7.28 (m, 4 H, Ar-H).
13C NMR (100 MHz, CDCl3): δ = 15.7 (d, J = 3.1 Hz, =CCH3), 21.5 and 21.6 (2 s, 2 CH3), 28.6 (d, J = 136.0 Hz, PCH3), 32.6 (d, J = 6.6 Hz, CMe2), 75.3 (d, J = 6.4 Hz, OCH3), 123.2 (d, J = 11.0 Hz, CMeH), 129.2, 129.3, 130.9, 131.7, 136.4 (d, J = 13.0 Hz, =CSAr).
31P NMR (160 MHz, CDCl3): δ = 21.5 (br s).

2-[2-(4-Chlorophenylsulfanyl)but-2-enyl]-1,3,2-dioxaphosphinane 2-Oxide (13b)

Yield: 0.24 g (45%); mp 117–119 °C.
IR (KBr): 1613, 1476, 1372, 1267, 1057, 1009 cm⁻¹.
1H NMR (400 MHz, CDCl3): δ = 1.04, 1.10 (2 s, 6 H, 2 CH3), 2.87 (d, J = 21.2 Hz, 2 H, PCH2) 3.83–4.23 (m, 4 H, OCH3), 5.16 and 5.51 (2 d, 2 H, J = 4.8 Hz, =CH2), 7.27–7.43 (m, 4 H, Ar-H).
13C NMR (100 MHz, CDCl3): δ = 21.5 and 21.6 (2 s, 2 CH3), 32.4 (d, J = 135.0 Hz, PCH2), 32.7 (d, J = 6.0 Hz, CMe2), 75.5 (d, J = 6.0 Hz, OCH2), 118.5 (d, J = 10.0 Hz, =CH3), 129.6, 130.8, 134.3 (d, J = 10.0 Hz, =CSAr), 134.6, 134.7.
31P NMR (160 MHz, CDCl3): δ = 20.5 (s).

2-[2-(4-Chlorophenylsulfanyl)but-1-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (12b) and 2-[2-(4-Chlorophenylsulfanyl)but-2-enyl]-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (13b)

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and the thiol gave IR (KBr): 3385 (br), 1649 (br), 1474, 1267, 1063, 1007 cm–1.

Anal. Calcd for C12H23O4PS: C, 48.97; H, 7.82, S, 10.91. Found: C, 48.92; H, 7.84; S, 10.91.


d the thiol gave IR (KBr): 3262, 2224, 1479, 1152, 1057, 1003 cm–1.


An X-ray crystal structure was determined for this sample.

2-(3-Hydroperoxy-3-methylbut-1-ynyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (15) and 2-(3-Hydroxy-3-methylbut-1-ynyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-Oxide (16); Typical Procedure

These two compounds were obtained by simply exposing the allenic 
 ca. 0.50 g, 2.3 mmol) to air for 30 d in an Erlenmeyer flask and they were separated by column chromatography (hexane–EtOAc, 1:1).

31P NMR (160 MHz, CDCl3): δ = 10.0 (s).

An X-ray crystal structure was determined for this sample.

2-(3-Hydroxy-3-methylbut-1-ynyl) Derivative 15

IR (KBr): 3262, 2224, 1479, 1152, 1057, 1003 cm–1.


An X-ray crystal structure was determined for this sample.

2-(3-Hydroxy-3-methylbut-1-ynyl) Derivative 16

Yield: 0.208 g (5%); Rf = 0.56 (hexane–EtOAc, 1:1); mp 120–122 °C.

IR (KBr): 3262, 2224, 1479, 1152, 1057, 1003 cm–1.


An X-ray crystal structure was determined for this sample.

2.06 g (50%); Rf = 0.56 (hexane–EtOAc, 1:1); mp 98–100 °C.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.

IR (KBr): 3364, 2205, 1478, 1464, 1377, 1279, 1183, 1128, 1051, 999 cm–1.
3-(4-Chlorophenylsulfanyl)-4-methyl-1-[4-toly]penta-1,3-diene (18a); Typical Procedure
The phosphonate 13d (0.20 g, 0.55 mmol) was dissolved in THF (10 mL) and slowly added to a suspension of NaH (0.05 g, 2.2 mmol) in THF (20 mL) at 0 °C over 5 min; the mixture was stirred at this temperature for 0.5 h. Then, 4-methylbenzaldehyde (0.06 g, 0.49 mmol) was added and the mixture stirred at r.t. for 6 h. H₂O (5 mL) was added and the aqueous layer extracted with Et₂O (3 × 10 mL). The organic layer was collected, dried (Na₂SO₄), and filtered. The solvent was removed to attain the residue that was purified by column chromatography (hexane–EtOAc) to give 18a; yield: 0.12 g (76%, based on the aldehyde used); mp 106–108 °C.

1H NMR (400 MHz, CDCl₃): δ = 2.18 (s, 6 H, 2 CH₃), 5.81 (m, J = 15.6 Hz, 1 H, =CH). 13C NMR (100 MHz, CDCl₃): δ = 13.6, 137.4, 146.9. IR (KBr): 1605, 1510, 1474, 1248, 1094, 968 cm⁻¹.

1,4-Bis-[3-(4-chlorophenylsulfanyl)-4-methylpenta-1,3-dienyl]benzene (20)
Following the typical procedure for 18a but in this case the mixture was heated under reflux for 6 h; yield: 0.08 g (56%); mp 190–192 °C (became reddish in color).

IR (KBr): 1610 (wv), 1474, 1092, 1011, 953, 808 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 2.19 [s, 12 H, 2 (CH₃)]; 6.96 (d, J = 15.3 Hz, 2 H, =CH), 7.07–7.31 (m, 16 H, Ar-H, =CH). 13C NMR (100 MHz, CDCl₃): δ = 21.7 and 24.9 (2 s, 2 CH₃), 124.5, 124.9, 126.8, 127.4, 128.9, 130.4, 131.1, 136.3, 136.8, 147.1.

Anal. Calcd for C₂₂H₁₈Cl₂S: C, 72.68; H, 5.82; S, 9.92. Found: C, 72.68; H, 5.39; S, 12.86.

2-([Benzazepaz-2-y])[4-sulfanyl]-3-methylbut-2-enyl]-5,5-dimethyl-1,3-dioxaphospholane 2-Oxide (130)
Following the typical procedure for 12a/13a using allene 1c (0.50 g, 2.3 mmol) and benzoxazol-2-thiol (0.42 g, 2.8 mmol) and heating for 20 h; yield: 0.542 g (64%); mp 82–84 °C.

IR (KBr): 1784, 1599, 1503, 1453, 1372, 1262, 1063, 1007 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 0.99, 1.05 (2 s, 6 H, 2 CH₃), 2.07 and 2.13 [2 d, 6 H, J = 5.0 Hz, =CH(CH₃)]; 3.34 (d, J = 20.0 Hz, 2 H, PCH₂), 3.78–4.20 (m, 4 H, OCH₂), 7.25–7.62 (m, 4 H, Ar-H).

13C NMR (100 MHz, CDCl₃): δ = 21.4 and 21.5 (2 s, 2 CH₃), 22.6 (d, J = 3.0 Hz, =CH₃), 24.2 (d, J = 3.0 Hz, =CH₃), 31.6 (d, J = 130.5 Hz, PCH₂), 32.6 (d, J = 5.9 Hz, CMe₂), 75.1 (d, J = 6.4 Hz, OCH₂), 110.0, 110.4 (d, J = 13.6 Hz, =CSAr), 118.7, 124.0, 124.3, 142.0, 150.2 (d, J = 11.0 Hz, =CMe₂), 151.9, 163.6. 31P NMR (160 MHz, CDCl₃): δ = 22.5 (s).

Anal. Calcd for C₃₀H₂₈Cl₂S: C, 68.81; H, 5.39; S, 12.86. Found: C, 68.82; H, 5.39; S, 12.92.

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grams. M.C. thanks CSIR for a fellowship.

References
(10) The $^1$H NMR spectrum of this mixture showed peaks at $\delta = 3.40$ (d, $J = 22.0$ Hz), in addition to those for 12a and 1a. There was also an additional minor peak in the initial stages in the $^{13}$P NMR at $\delta = 23.9$ (unassigned).
(11) Compound 15 was more difficult to obtain in a pure form, probably because of conversion into 16.
(12) When we tried to separate this compound from 5,5-diethyl-2-(3-methylbuta-1,2-dienyl)-1,3,2-dioxaphosphinane 2-oxide using column chromatography, a small quantity of an additional species [6(P)–12.2] was noticed in a few fractions.
(13) sanders, w.; patyk, a. angew. chem., int. ed. engl. 1987, 26, 475; and references cited therein.
(14) Such trienes are perhaps useful in cyclization reactions, see: murahashi, t.; nakashima, h.; nagai, t.; mino, y.; okuno, t.; jili, m. a.; kurosawa, h. j. am. chem. soc. 2006, 128, 4377; and references cited therein.
(17) (b) guillemin, j. c.; savignac, p.; denis, j. m. angew. chem., int. ed. engl. 1987, 26, 475; and references cited therein.
(19) (a) satish kumar, n. ph.d. thesis; university of hyderabad: india, 2004. (b) guillemin, j. c.; savignac, p.; dennis, j. m. inorg. chem. 1999, 38, 5317. (c) sheldrick, g. m. sadabs, siemens area detector absorption correction; university of göttingen: germany, 1998. (d) sheldrick, g. m. shelixlt/n crystal structure analysis package, version 5.10; bruker axs, analytical x-ray system: wi usa, 1999.