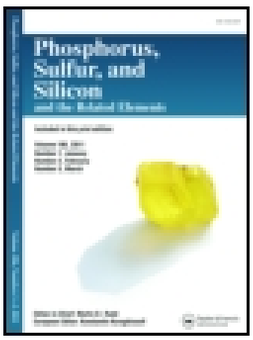


Taylor & Francis
Taylor & Francis Group

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

Reaction of allenylphosphonates/allenylphosphine oxides with thiocyanates/isothiocyanates or oxalyl Chloride/$AgNo_3$

K. C. Kumara Swamy, Manab Chakravarty, Shubham Debnath & M. Nagarjuna Reddy

To cite this article: K. C. Kumara Swamy, Manab Chakravarty, Shubham Debnath & M. Nagarjuna Reddy (2017): Reaction of allenylphosphonates/allenylphosphine oxides with thiocyanates/isothiocyanates or oxalyl Chloride/$AgNo_3$, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2017.1287707

To link to this article: http://dx.doi.org/10.1080/10426507.2017.1287707

Accepted author version posted online: 13 Feb 2017.

REACTION OF ALLENYLPHOSPHONATES/ALLENYLPHOSPHINE OXIDES WITH THIOCYANATES/ISOTHIOCYANATES OR OXALYL CHLORIDE/$AgNO_3$

K. C. Kumara Swamy[a,*], Manab Chakravarty[a,b], Shubham Debnath[a] and M. Nagarjuna Reddy[a]

[a]School of Chemistry, University of Hyderabad, Hyderabad- 500046, Telangana, India

[b]Current address: Department of Chemistry, Birla Institute of Technology & Science, Pilani Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, Hyderabad 500 078, Telangana, India

[*]Corresponding Author E-Mail: kckssc@uohyd.ac.in

Abstract

In this paper, we describe thiocyanation as well as chlorination of selected allenylphosphonates/allenyl phosphine oxide, using ammonium thiocaynate or $(OCH_2CMe_2CH_2O)PNCS$ (for thiocyanation) or oxalyl chloride/$AgNO_3$ for chlorination. The resulting products are vinyl (thiocyanato)phosphonates or vicinal dichloro(vinyl) phosphonates. One of the vinyl thiocyanato-phosphonates is characterized by single crystal X-ray crystallography.

Keywords

Allenes; Allenylphosphonates; Allenylphosphine oxides; vinyl thiocyanato-phosphonate, vicinal dichloro vinylphosphonates

Dedication: This paper is dedicated to Prof. *Harry R. Hudson* in recognition of his contributions to phosphorus chemistry

INTRODUCTION

Allenylphosphonates can be utilized as versatile intermediates in organic synthesis for diverse transformations owing to their ready availability, stability and low cost of preparation.[1] A variety of substituted vinylphosphonates and allylphosphonates, β-keto- and β-amino-phosphonates and phosphorus substituted heterocycles have been synthesized by starting with allenylphosphonates/allenylphosphine oxides.[1-3] Phosphorus based allenes **1**-**2** (cf. Chart 1) are useful substrates to explore the chemistry of non-phosphorylated allenes because of the feasibility of easy monitoring the progress of the reaction by ^{31}P NMR spectroscopy.[4] Halogenation/pseudohalogenation of allenes can lead to new vinyl substituted products that could further be functionalized. Direct halogenation of phosphorus-based allenes using chlorine/bromine/iodine has been known, but not exhaustively.[5-6] Using $AgNO_3/(COCl)_2$, Vankar and co-workers described a simple method for the chloroamidation of olefins.[7] Whether similar reaction occurs with phosphorus-based allenes or not is one of interests in this work. As regards 'pseudohalogenation', a few reports of azidation have been documented.[8-9] A couple of interesting reports on azidation from our group are shown in Scheme 1.[8-9] To our knowledge, studies to incorporate other pseudohaogens appear rather nonexistent. In this communication, we report some results on the thiocyanic acid addition to allenylphosphonates/allenylphosphine oxides. X-ray structure of one such product is also reported herein. Later, we report the chlorination that in contrast to the chloroamidation reaction using alkenes, chlorination takes place when allenylphosphonates are utilized.

RESULTS AND DISCUSSION

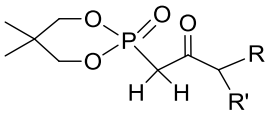
1. Reaction of Phosphorus-Based Allenes with ($OCH_2CMe_2CH_2O$)P-NCS (4) or Ammonium Thiocyanate- Formation of Vinyl Thiocyanatophosphonates / Thiocyanatophosphine oxides or β-Ketophosphonates

The isothiocyanato phosphite ($OCH_2CMe_2CH_2O$)PNCS (**4**) is prepared by reacting **3** with potassium thiocyanate in acetonitrile (Scheme 2). The nitrogen end, and not the sulfur end, is connected to phosphorus on the basis of the observation that the X-ray structure of corresponding 8-membered ring compound CH_2(6-*t*-Bu-4-Me-$C_6H_4O)_2$P-NCS, prepared by a similar method, is known.[10] An interesting feature of compound **4** is that in the ^{31}P NMR spectrum, the $^1J(^{31}P\text{-}^{14}N)$ coupling is observed. It should be noted that in a majority of compounds with P-N bond this coupling is not observed.

Upon treating allenes **5a-c** with *isothiocyanate* **4**, we obtained the vinyl(*thiocyanato*)phosphonates **6a-c**. Since the H-phosphonate **7** is also isolated in this reaction, we believe that adventitious moisture is involved in this reaction. It can be noted that in the preparation of vinyl azides from the reaction of Me_3SiN_3 also, a similar observation is made. What is interesting in the case of our reaction is that while the *N*-end (isothiocyanate) is connected to phosphorus in **4**, it is the *S*-end (thiocyanate) that is connected in **6a-c**. The presence of thiocyanate grouping in **6a-c** is clearly shown in the IR spectrum [a band at 2157 cm^{-1}]. The other groups were also clearly established by multinuclear NMR. The X-ray structure of compound **6a** is shown in Figure 1. In the case of **6b**, as expected, both *E* and *Z* isomers are formed (ratio ~ 7/3).

It is likely that the above addition takes place via HSCN resulting from the hydrolysis of ($OCH_2CMe_2CH_2O$)PNCS (**4**) due to the presence of adventitious moisture. As an alternative

source of HSCN, we chose ammonium thiocyanate (NH_4SCN; dried *in vacuum* for 2 h), in acetonitrile or tetrahydrofuran medium for the above reaction with **5a**. Here, the ^{31}P NMR spectrum of the reaction mixture showed two peaks at δ 17.7 (55%, compound **6a**) and δ 14.3 (45%). The latter peak is due to the *β*-ketophosphonate $(OCH_2CMe_2CH_2O)P(O)CH_2C(O)CH_3$ (**8**) that could arise due to addition of water to **6a**.[11,12] Potassium thiocyanate did not react with the allene. The reaction of allene **5b** with NH_4SCN led to a considerable amount of the *β*-ketophosphonate $(OCH_2CMe_2CH_2O)P(O)CH_2C(O)CH_2CH_3$ (**9**).[11] Allene **5c** gave better yields (60%) of the addition product **6c** along with the *β*-ketophosphonate $(OCH_2CMe_2CH_2O)P(O)CH_2C(O)CH(CH_3)_2$ (**10**).[11]



R, R' = H [**8**; δ(P): 17.6]
R = Me, R' = H [**9**; δ(P):19.2]
R, R' = Me [**10**; δ(P): 20.7]

In a manner similar to the above, but by using NH_4SCN, we have also been able to synthesize (thiocyanato)vinyl phosphine oxides **12a-c** by starting with the allenylphosphine oxides **11a-c** (Scheme 4).[11,13] Compound **4** was not effective for the conversion in these cases. Although the corresponding β-keto products were also present, isolation of the required products could be accomplished readily in the case of **12a-b**. In the case of compound **12c**, because of the closeness of the tlc R_f value with the minor product (possibly the β-keto product), it could be isolated only in 70% purity; the yield of the product initially was >50% (NMR evidence).

2. Reaction of Phosphorus-Based Allenes with Oxalyl Chloride/$AgNO_3$ System

The basis for attempting this reaction was to have an analogy with that in the literature between alkenes and $AgNO_3$/oxalyl chloride under similar conditions. Using $AgNO_3/(COCl)_2$ Vankar and co-workers described a simple method for the chloroamidation of olefins (Scheme 5).[7] In this reaction, acetonitrile acted both as the solvent and as the reagent.

The reaction of allenylphosphonates **13-15** with oxalyl chloride and $AgNO_3$ led to a mixture of products (**16a-c**, **17a** and **18a-c)** (Scheme 5). In these cases, oxalyl chloride acted as a chlorine source (acetyl chloride failed to react). The reaction involves addition of two chlorine atoms across double bond of allene to lead to three distinct isomeric products in the reaction using **13** (cf. Figure 2). Only compounds **16a**, **17a**, **18a** and **18b** could be isolated in a pure state. Thus it should be noted that the reaction of $AgNO_3/(COCl)_2$ with allenes proceeds in a manner different from that with alkenes. The assignment of structures is based on NMR and HRMS data. As an example, compound **16a** shows two singlets at δ 5.79 and 6.34 in the ^{1}H NMR spectrum corresponding to geminal alkene protons and a doublet for P*C* carbon at δ 75.5 [^1J(PC) = 152.0 Hz] in the ^{13}C NMR spectrum for the P-*C*(sp^3) carbon. Compound **18b** shows a singlet at δ 4.05 in ^{1}H NMR due to CH_2 protons; a doublet at δ 132.4 [^1J(PC) = 175.0 Hz] in the ^{13}C NMR indicates the presence of P-*C* = C moiety. The molecular identity (two chlorine patterns) of the isolated compounds is also confirmed by HRMS data. The basis for the assignment of isomers **16c** and **18c** stems from literature reports on the reaction of nonphosphorus-allenes with $(COCl)_2$/ $[BnEt_3N][MnO_4]$.[14] In earlier literature reports on the direct chlorination (by Cl_2) of allenylphosphine oxides heterocyclic phosphonium salt **19** (Scheme 7a) was isolated, but in one case, vicinal dichlorovinylphosphine oxides were identified (but not isolated) by NMR spectroscopy.[6a] In another report, only compound **20** that is analogous to **16b-18b** (or **16c-18c**)

were identified (Scheme 7b).[6b] These products, however, were different from those contemplated in our initial objective.

CONCLUSIONS

In this preliminary report, we have shown that allenylphosphonates react with isothiocyanato substituted phosphites to lead to vinyl(thiocyanato)phosphonates. Such vinyl(thiocyanato)phosphonates may also be prepared directly by the reaction of allenes with ammonium thiocyanate. The yields are moderate, but the products could be synthetically valuable in view of the reactive thiocyanate and alkene moiety. This reaction appears to occur in the presence of adventitious moisture in a manner similar to that with trimethylsilyl azide. The structure of one such thiocyanato compound has been confirmed by single crystal X-ray crystallography. However, a competitive reaction leading to β-ketophosphonates is also formed, depending on the allenylphosphonate/allenylphosphine oxide used.

In contrast to the reaction of $AgNO_3$/oxalyl chloride with normal olefins wherein chloroamidation occurs,[7] the analogous reaction with allenes give only vicinal dichloro vinylphosphonates. Many such vicinal (dichloro)vinylphosphonates have been isolated and characterized in the present study.

Experimental Section

Chemicals were purified when required according to standard procedures.[15] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using 5 mm tubes on 200, 400 or on 500 MHz spectrometer with field strengths 200/50/80, 400/100/160 or 500/125/202 MHz, respectively in $CDCl_3$ solution with shifts

referenced to $SiMe_4$ or ext. 85% H_3PO_4 (δ = 0). All *J* values are in Hz. Infrared spectra were recorded neat or by using KBr pellets on a FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. For TLC, glass micro slides were coated with silica-gel-GF_{254} (mesh size 75μ) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100-200 mesh size was used. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. Details of spectra are available with the authors.

(i) Synthesis of the isothiocyanate compound 4

The precursor $(OCH_2CMe_2CH_2O)PCl$ (**3**) [16] (3.58 g, 16.0 mmol) was stirred with potassium thiocyanate (4.6 g, 48.0 mmol) in dry acetonitrile for 4 d at room temperature (25 °C). Then, the solvent was removed under vacuum; the required compound **4** was extracted with dry hexane and purified by vacuum distillation. Yield: Quantitative. Bp: 80-90 ^oC (16 mm Hg). ^1H NMR (400 MHz): δ 0.81 and 1.24 (2 s, 6 H, $CH(CH_3)_2$), 3.55 (dd → t, *J*(PH) ~ *J*(HH) ~10.5 Hz each, 2 H, -OCH_2), 4.11 (dd → t, *J*(PH) ~ *J*(HH) ~10.5 Hz each, 2 H, OCH_2). ^{13}C NMR (50 MHz):δ 22.3, and 22.6 (2 s, $CH(CH_3)_2$), 32.9 (d, *J*(PC) = 4.0 Hz, CMe_2), 72.0 (br, OCH_2), 146.8 (br, -NCS). ^{31}P NMR (80 MHz): δ 105.5 (t, *J*(PN) ~ 66.0 Hz). LCMS: *m/z* 191. This compound was hydrolytically unstable.

***(ii) Reaction of 5a with 4: Preparation of* $(OCH_2CMe_2CH_2O)P(O)CH_2C(SCN) = CH_2$ (6a)**

To a solution of **5a** (0.20 g, 1.06 mmol) in dry THF $(OCH_2CMe_2CH_2O)PNCS$ (**4**) (0.40 g, 2.12 mmol) was added via syringe. The reaction mixture was heated under reflux for 24-48 h.

The reaction mixture ^{31}P NMR showed mainly two peaks: one at δ 17.9 (product) and the second at δ 1.1 that corresponded to $(OCH_2CMe_2CH_2O)P(O)H$. The reaction mixture was washed with water (3×50 mL) and extracted with ether (3×25 mL). After the removal of solvent from the extract, and subjecting the residue to column chromatography (EtOAc/hexane 1/1; silica gel) afforded **6a** that was then crystallized from CH_2Cl_2-hexane (1:1) mixture. Yield: 0.21 g (80%). Mp:108-110 °C. IR (KBr): 2159, 1618, 1476, 1261, 1055, 1007 cm^{-1}. ^{1}H NMR (200 MHz): δ 1.07 and 1.13 (2 s, 6 H, $C(CH_3)_2$)), 3.05 (d, *J*(PH) = 21.1 Hz, 2 H, PCH_2), 3.93 (dd → t, *J*(PH) ~ *J*(HH)~12.0 Hz each, 2 H, OCH_2), 4.24 (dd → t, *J*(PH) ~ *J*(HH) ~ 12.0 Hz each, 2 H, OCH_2), 5.80-5.83 (m, 2 H, = CH_2). ^{13}C NMR (50 MHz): δ 21.4 and 21.5 (2 s, $C(CH_3)_2$), 32.3 (d, *J*(PC) = 134.9 Hz, PCH_2), 32.6 (d, *J*(PC) = 6.5 Hz, $C(CH_3)_2$), 75.9 (d, *J*(PC) = 6.0 Hz, OCH_2), 109.5 (s, SCN), 124.3 (d, *J*(PC) = 9.9 Hz, = CH_2), 124.7 (d, *J*(PC) = 11.2 Hz, PC-*C*). ^{31}P NMR (80 MHz): δ 17.6. Anal. Calcd. for $C_9H_{14}O_3PNS$: C, 43.72; H, 5.70; N, 5.66; S, 12.97. Found: C, 43.70; H, 5.70; N, 5.74; S, 12.88. X-ray structure was determined for this sample.

***(iii) Preparation of* (OCH$_2$CMe$_2$CH$_2$O)P(O)CH$_2$C(SCN) = CH(Me) (6b- isomeric mixture)**

This compound was prepared as a mixture of isomers (*E*:*Z* = 7:3) using a procedure similar to that for **6a** using **5b** with the same molar quantities of reactants. Yield: 0.13 g (50%). Mp: 72-74 °C. IR (KBr): 2157, 1478, 1263, 1057, 1005 cm^{-1}. ^{1}H NMR (200 MHz, major isomer, ca 85%): δ 1.05 and 1.11 (2 s, 6 H, $C(CH_3)_2$)), 1.94--1.96 (m, 3 H, = $C(CH_3)$, 3.10 (d, *J*(PH) = 20.5 Hz, 2 H, PCH_2), 3.89-3.95 (m, 2 H, OCH_2), 4.20--4.25 (m, 2 H, OCH_2), 6.32--6.35 (m, 1 H, = CH). ^{13}C NMR (50 MHz): δ 16.4 (s, = $C(CH_3)$), 21.4 and 21.5 (2 s, $C(CH_3)_2$), 32.6 (br, $C(CH_3)_2$), 33.5 (d, *J*(PC) = 136.0 Hz, PCH_2), 75.7 (d, *J*(PC) = 6.1 Hz, OCH_2), 110.2, 115.6

(S*C*N), 139.0 (d, *J*(PC) = 9.9 Hz). ^{31}P NMR (80 MHz): δ 19.2. For the minor isomer, other peaks (ca~ 15%) at δ 1.03, 1.12, 1.86-1.89 (m), 6.29- 6.30 (m) in the ^{1}H NMR and a peak at δ 19.4 in ^{31}P NMR spectra were observed. Anal. Calcd. for $C_{10}H_{16}O_3PNS$: C, 45.96; H, 6.17; N, 5.36. Found: C, 45.94; H, 6.18; N, 5.30.

***(iv) Preparation of* (OCH$_2$CMe$_2$CH$_2$O)P(O)CH$_2$C(SCN) = CMe$_2$ (6c)**

The procedure and molar quantities were the same as that for **6a**. Yield: 0.144 g (60%). Mp: 64-66 °C. IR (KBr): 2151, 1680, 1474, 1273, 1061, 1011 cm^{-1}. ^{1}H NMR (200 MHz): δ 1.04 and 1.13 (2 s, 6 H, C(C*H*$_3$)$_2$)), 2.01 and 2.11 (2 d, *J*(HH) ~ 5.0 Hz each, 6 H, = C(C*H*$_3$)$_2$), 3.18 (d, *J*(PH) = 20.8 Hz, 2 H, PC*H*$_2$), 3.92 (dd → t, *J*(PH) ~ *J*(HH) ~ 11.2 Hz each, 2 H, OC*H*$_2$), 4.24 (dd → t, *J*(PH) ~ *J*(HH) ~11.2 Hz each, 2 H, OC*H*$_2$). ^{13}C NMR (50 MHz): δ 21.4, 21.5, 22.6 and 22.4 (4 s, C(*C*H$_3$)$_2$ + = C(*C*H$_3$)$_2$), 31.3 (d, *J*(PC) = 138.3 Hz, P*C*H$_2$), 32.7 (br, *C*(CH$_3$)$_2$, signals are merged with P*C*H$_2$), 75.4 (d, *J*(PC) = 6.1 Hz, O*C*H$_2$), 107.6 (d, *J*(PC) = 14.6 Hz), 110.8 (S*C*N), 149.0 (d, *J*(PC) = 10.9 Hz). ^{31}P NMR (80 MHz): δ 20.7. Anal. Calcd. for $C_{11}H_{18}O_3PNS$: C, 47.99; H, 6.59; N, 5.08; S, 11.64. Found: C, 47.95; H, 6.56; N, 5.16; S, 11.64.

***(v) Preparation of* Ph$_2$P(O)CH$_2$C(SCN) = CRR' (12a-c)**

A mixture of NH_4SCN (2 equiv) and the allenylphosphine oxide (one equiv) was heated under reflux in THF (ca 1 mL/1 mmol of allene) for 12 h. After removal of the solvent, dichloromethane (2 mL) was added to the residue and the soluble portion was column chromatographed (acetone/hexane 1/1; silica gel) to obtain one of **12a-c**.

Compound 12a (0.208 mmol of allene **11a** [δ(P) 24.6] was used)**:** Yield: 30 mg (60%), Mp: 114-116 °C. IR (KBr): 2926, 2151, 1609, 1433, 1170, 1128, 1092, 1066, 896, 844, 746, 725, 700

cm^{-1}. ^{1}H NMR (500 MHz): δ 3.44 (d, *J* = 13.0 Hz, 2H, -PCH_2), 5.70-5.74 (m, 2H, = CH_2), 7.51-7.54 (m, 4H, Ar-*H*), 7.77- 7.81 (m, 4H, Ar*H*), 7.58-7.59 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz): δ 37.9 (d, *J* = 52.0 Hz, -P*C*), 109.9, 124.6_6, 124.7_2, 125.1_6, 125.2_4, 128.9, 129.0, 130.8, 130.9, 131.0, 131.6, 132.5, 132.5. ^{31}P NMR (202 MHz): δ 27.28. HRMS (ESI): Calcd. for $C_{16}H_{15}NOPS$ [M^++H]: *m/z* 300.0612. Found: 300.0607.

Compound 12b (0.79 mmol of allene **11b** [δ(P) 25.1] was used)**:** Yield: 83 mg (42%), Mp: 108-110 °C, IR (KBr): 3057, 2916, 2152, 1636, 1590, 1484, 1438, 1403, 1334, 1199, 1120, 998, 951, 833, 743, 722, 696, 565 cm^{-1}. ^{1}H NMR (500 MHz): δ 1.71-1.74 (m, 3H, CH_3), 3.52 (d, *J* = 12.5 Hz, 2H, -PCH_2), 6.35-6.37 (qrt, 1H, = *CH*), 7.51-7.54 (m, 4H, *ArH*), 7.58 (t, *J* = 10.0 Hz, 2H, *Ar-H*), 7.80-784 (m, 4H, *Ar-H*). The amount of the other possible stereo-isomer was <1%. ^{13}C NMR (125 MHz): δ 16.0 (d, *J* = 10.0 Hz, -CH_3), 34.4 (d, *J* = 65.0 Hz, -P*C*), 111.2_6 111.2_7, 115.7, 115.8, 128.8, 128.9, 130.9_1, 131.0_1, 131.3, 132.2_8, 132.3_7, 132.40, 140.1, 140.2. ^{31}P NMR (202 MHz): δ 26.91. HRMS (ESI): Calcd. for $C_{17}H_{16}NOPSNa$ [M^++Na]: *m/z* 336.0588. Found: 336.0585.

Compound 12c (purity ca 70% only) (0.75 mmol of allene **11c** [δ(P) 27.1] was used)**:** Yield: ca 80 mg (~40% for the expected compound; although initially it was >50%, the yield became lower during separation), Mp: ~122 °C, IR (KBr): 3056, 2915, 2150 (SCN), 1958, 1438, 1197, 1120, 794, 737 cm^{-1}. ^{1}H NMR (500 MHz): δ 1.82 and 2.06 (two s, 6H, CH_3), 3.60 (d, *J* = 12.0 Hz, 2H, -PCH_2), 7.30-7.83 (m, ca 10 H, *ArH*). For the minor product, signals were observed at δ 1.55 and 5.68 (br m) in addition to the signals for the aromatic protons. ^{13}C NMR (125 MHz): δ 22.7 (d, *J* = 2.0 Hz)) and 24.1 (d, *J* = 2.0 Hz), 36.8 (d, *J* = 53.0 Hz, -P*C*), 97.6 (d, *J* = 19.0 Hz),

108.2 (d, *J* = 9.0 Hz), 111.3 (S*C*N), 128.7 (*J* = 9.4 Hz), 131.0 (*J* = 7.4 Hz), 132.5, 149.5 (d, *J* = 6.8 Hz). Signals for the minor product were observed at 18.8 (d, *J* = 4.6 Hz, -CH_3), 83.6 (*J* = 85.3 Hz) and 210.9 along with peaks for Ar-*C* nuclei and hence the full analysis was not made.. ^{31}P NMR (202 MHz): δ 27.2 (minor product signal at 26.0). HRMS (ESI): Calcd. for $C_{18}H_{18}NOPSNa$ [M^++H]: *m/z* 328.0923. Found: 328.0924.

(vi) Synthesis of vicinal dichloro(vinyl)phosphonates 16a, 17a and 18a-b

To a suspension of silver nitrate (1.5 mmol) in dry CH_3CN (4 mL) was added oxalyl chloride (1.5 mmol) drop-wise *via* syringe at 0 °C. After 5 min, one of the allenylphosphonates **13-15**[11,13] (1.0 mmol) was added and the contents were stirred for 3 h at 0 °C. The reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (4×10 mL). The collected organic layers were washed with brine solution (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was subjected to column chromatography to afford the products **16a, 17a** and **18a-b**.

Compound 16a: Yield: 0.127 g (38%); Mp: 136-138 °C; IR (KBr): 2978, 1822, 1622, 1545, 1487, 1261, 1154, 1065, 1022, 901, 829, 710, 542 cm^{-1}; ^{1}H NMR (400 MHz): δ 0.80 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 4.02-4.20 (m, 4H, 2 OCH_2), 5.80 (s, 1H, = C$H_a$$H_b$), 6.36 (s, 1H, = C$H_a$$H_b$), 7.39-7.44 (m, 3H, Ar-*H*), 7.69-7.72 (m, 2H, Ar-*H*). ^{13}C NMR (100 MHz): δ 20.6, 22.1, 32.8 (d, *J* = 10 Hz), 75.5 (d, *J* = 152.0 Hz), 80.0 (dd→t, *J* = 10.0 Hz), 120.8, 128.2, 128.7, 129.0, 134.2, 138.7 (d, *J* = 12.0 Hz). ^{31}P NMR (160 MHz): δ 3.8. HRMS (ESI): Calcd. for $C_{14}H_{17}Cl_2NaO_3P$ [M^++Na]: *m/z* 357.0190, 359.0348 and 361.0179. Found: 357.0186, 359.0156 and 361.0121.

Compound 17a: Yield: 0.25 g (70%); Mp: 116-118 °C; IR (KBr): 2964, 1825, 1611, 1501, 1463, 1255, 1178, 1063, 1025, 910, 822, 762, 537 cm^{-1}. ^{1}H NMR (400 MHz): δ 0.84 (s, 3H, C*H*$_3$), 1.27 (s, 3H, C*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 3.91-4.25 (m, 4H, 2 OC*H*$_2$), 5.78 (s, 1H, = C*H*$_a$H$_b$), 6.33 (s, 1H, = CH$_a$*H*$_b$), 6.92 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.60 (dd, *J* = 8.8 and 2.0 Hz, 2H, Ar-*H*). ^{13}C NMR (100 MHz): δ 20.6, 22.1, 32.8 (d, *J* = 8.0 Hz), 55.3, 75.2 (d, *J* = 153.0 Hz), 79.9 (dd→t, *J* = 10.0 Hz), 113.6, 120.5, 126.0, 130.0, 138.9 (d, *J* = 10.0 Hz), 160.0. ^{31}P NMR: δ 4.1 (160 MHz). HRMS (ESI): Calcd. for $C_{15}H_{20}Cl_2O_4P$ [M^++H]: *m/z* 365.0477, 367.0635 and 369.0793. Found: 365.0479, 367.0450 and 369.0419.

Compounds 18a and 18b: The separation was done using hexane-ethyl acetate mixture [3:2 ratio for **18a** and 2:3 ratio for **18b**] as the eluent. **18a:** Yield: 0.092 g (25%). Mp: 130-132 °C. IR (KBr): 2964, 1825, 1611, 1501, 1463, 1255, 1178, 1063, 1025, 910, 822, 762, 537 cm^{-1}. ^{1}H NMR (400 MHz): δ 0.88 (s, 3H, C*H*$_3$), 1.28 (s, 3H, C*H*$_3$), 4.02-4.37 (m, 4H, 2 OC*H*$_2$), 5.79 (s, 1H, = C*H*$_a$H$_b$), 6.34 (s, 1H, = CH$_a$*H*$_b$), 7.37-7.39 (m, 2H, Ar-*H*), 7.62-7.64 (m, 2H, Ar-*H*). ^{13}C NMR (100 MHz): δ 20.7, 22.2, 33.0 (d, *J* = 10.0 Hz), 75.2 (d, *J* = 151.0 Hz), 80.2 (dd→t, *J* ~ 10.0 Hz), 121.0, 128.4, 130.2, 132.9, 135.2, 138.4 (d, *J* = 12.0 Hz). ^{31}P NMR (160 MHz): δ 3.5. HRMS (ESI): Calcd. for $C_{14}H_{17}Cl_3O_3P$ [M^++H]: *m/z* 368.9982, 371.0140, 373.0298 and 375.0456. Found: 368.9983, 370.9952, 372.9928 and 374.9909. **18b:** Yield: 0.155 g (42%). Mp: 142-144 °C. IR (KBr): 2970, 2882, 1595, 1474, 1267, 1063, 1008, 975, 838, 794, 526 cm^{-1}. ^{1}H NMR (400 MHz): δ 0.83 (s, 3H, C*H*$_3$), 1.18 (s, 3H, C*H*$_3$), 3.68 (dd, *J* = 11.2 and 6.8 Hz, 2H, OC*H*$_2$), 3.92 (dd, *J* ~ 17.2 and 11.2 Hz, 2H, OC*H*$_2$), 4.05 (s, 2H, C*H*$_2$), 7.32 (dd, *J* ~ 8.8 and 2.0 Hz, 2H, Ar-*H*), 7.41 (d, *J* = 8.8 Hz, 2H, Ar-*H*). ^{13}C NMR (100 MHz): δ 20.9, 21.7, 32.3 (d, *J* =

7.0 Hz), 46.3 (d, *J* = 14.0 Hz), 76.5, 76.6, 129.3, 130.0 (d, *J* = 5.0 Hz), 131.5, 132.4 (*J* = 175.0 Hz), 135.3, 144.1. ^{31}P NMR (160 MHz): δ 4.4. HRMS (ESI): Calcd. for $C_{14}H_{16}Cl_3NaO_3P$ [M^++Na]: *m/z* 390.9801, 392.9959 and 395.0117. Found: 390.9803, 392.9778 and 394.9747.

X-ray data for compound 6a [CCDC: 1524604] was collected at 293 K on a Bruker AXS-SMART diffractometer using Mo-K_α radiation (λ = 0.71073 Å) using standard methods.[17] Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: + 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.can.ac.uk). Crystal data for compound **6a**: Emp. formula $C_9H_{14}NO_3PS$; Formula weight 247.24; Crystal system Monoclinic; Space group P2(1)/c; *a* /Å 6.7093(5); *b* /Å 17.4433(12); *c* /Å 11.1154(7); *β*/deg 102.2960(10); *V* /Å^3 1271.02(15); *Z* = 4; D_{calc} /g cm^{-3} 1.292; μ /mm^{-1} 0.369; *F*(000) 520; Data/ restraints/ parameters 2225 / 0/ 138; S 1.061; R1 [I>2σ (I)] 0.0475; wR2 [all data] 0.1334; Max./min. residual electron dens. [eÅ^{-3}] 0.195/ - 0.351

ACKNOWLEDGMENTS:

We thank Council of Scientific and Industrial Research (CSIR), Department of Science and Technology (DST-FIST and PURSE), and University Grants Commission (UGC-UPE-2) for financial support.

REFERENCES

1. Selected references: (a) Khusainova, N. G.; Pudovik, A. N. *Russ. Chem. Re*v. **1987**, *56*, 564 (review) (b) Alabugin, I. V.; Brel, V. K. *Russ. Chem. Re*v. **1997**, *66*, 205 (c) Bhuvan Kumar, N. N.; Nagarjuna Reddy, M.; Kumara Swamy, K. C. *J. Org. Chem*. **2009**, *74*, 5395-5404 (d) Pavan, M. P.; Reddy, M. N.; Kumar, N. N. B.; Kumara Swamy, K. C. *Org. Biomol. Chem*., **2012**, *10*, 8113-8118 (e) Siva Kumari, A. L.; Srinivas, V.; Kumara Swamy, K. C. *J. Chem. Sci*. **2013**, *125*, 1405-1417 (f) Gangadhararao, G.; Kotikalapudi, R.; Reddy M. N.; Kumara Swamy K. C. *Beilstein J. Org. Chem.* **2014**, *10*, 996-1005 (g) Anitha, M.; Gangadhararao, G.; Kumara Swamy, K. C. *Org. Biomol. Chem*. **2016**, *14*, 3591-3602 (h) Nagaraju, K.; Kumara Swamy, K. C. *Org. Biomol. Chem*. **2016**, *14*, 5079-5087. i) Srinivas, V.; Sajna, K. V.; Kumara Swamy, K. C. *Chem. Commun.* **2011**, *47*, 5629-5631. (j) Sajna, K. V.; Kumara Swamy, K. C. *J. Org. Chem.* **2012**, *77*, 5345-5356.
2. (a) Baumann, M.; Baxendale, I. R. *J. Org. Chem.* **2015**, *80*, 10806-10816 (b) Bogachenkov, A. S.; Dogadina, A. V.; Boyarskava, I. A.; Boyarskiy, V. P.; Vasilyev, A. V. *Org. Biomol. Chem.* **2016**, *14*, 1370-1381 (c) Ye, J.; Ma, S. *Acc. Chem. Res*. **2014**, *47*, 989-1000 (d) Panossian, A.; Fleury-Bregeot, N.; Marinetti, A. *Eur. J. Org. Chem.* **2008**, 3826-3833 (e) He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035-8042 (f) He, G.; Yu, Y.; Fu, C.; Ma, S. *Eur. J. Org. Chem.* **2010**, 101-110 (g) Pinto, N.; Neel, M.; Panossian, A.; Retailleau, P.; Frison, G.; Voituriez, A.; Marinetti, A. *Chem. Eur. J.* **2010**, *16*, 1033-1045 (h) Xin, N.; Ma, S. *Eur. J. Org. Chem.* **2012**, 3806-3817 (i) Chen, Y-Z.; Zhang, L.; Lu, A-M.; Yang, F.; Wu, L. *J. Org. Chem.* **2015**, *80*, 673-680 (j) Mazzuca, D.; Angelov, C.; Wiebe, L. I. *J. App. Pharm. Sci.*

2015, *5(11)*, 001-009 (k) Guo, H.; Yu, F.; Ma, S. *J. Org. Chem.* **2006**, *71*, 6634-6636 (l) Yu, F.; Lian, X.; Ma, S. *Org. Lett.* **2007**, *9*, 1703-1706.

3. (a) Panossian, A.; Fleury-Bregeot, N.; Marinetti, A. *Eur. J. Org. Chem.* **2008**, 3826. (b) Brel, V. K.; Belsky,V. K.; Stash, A. I.; Zavodnik, V. E.; Stang. P. J. *Org. Biomol. Chem*. **2003**, *1*, 4220 (c) Brel, V. K.; Belsky,V. K.; Stash, A. I.; Zavodnik, V. E.; Stang. P. J. *Eur. J. Org. Chem.* **2005**, 512 (d) Zhang, M. L.; Chen, Y.-Z.; Zhu, J.; Wu, L. *ACS Catal.* **2017**, *7*, 181−185.
4. (a) Sajna, K. V.; Kotikalapudi, R.; Chakravarty, M.; Bhuvan.Kumar, N. N.; Kumara Swamy, K. C. *J. Org. Chem*. **2011**, *76*, 920-938 (b) Chakravarty, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2006**, *71*, 9128-9138 (c) Srinivas, V.; Balaraman, E.; Sajna, K. V.; Kumara Swamy, K. C. *Eur. J. Org. Chem*. **2011**, 4222-4230.
5. (a) Christov, V. C.; Prodanov, B. *Phosphorus, Sulfur Silicon Relat. Elem.*, 2002, 177, 243–249 (a) Guo, H.; Qian, R.; Guo, Y.; Ma, S. *J. Org. Chem.* **2008**, *73*, 7934-7938 and references cited therein/(b) Ma, S. *Acc. Chem. Res.*, **2009**, *42*, 1679–1688 .
6. (a) Angelov, C. M. *Phosphorus and Sulfur*, **1983**, *15*, 177-183. (b) Angelov, C. M. *Phosphorus and Sulfur*, **1988**, *37*, 125-128.
7. Rawal, G. K.; Kumar, A.; Tawar, U.; Vankar, Y. D. *Org. Lett*. **2007**, *9*, 5171-5174.
8. Chakravarty, M.; Bhuvan Kumar, N. N.; Sajna, K. V.; Kumara Swamy, K. C. *Eur. J. Org. Chem.* **2008**, 4500–4510.
9. Sajna, K. V.; Kumara Swamy, K. C. *J. Org. Chem.* **2012**, 77, 8712-8722.
10. Kumaraswamy, S.; Senthil Kumar,K.; Satish Kumar, N.; Kumara Swamy, K. C. *Dalton Trans.* **2005**, 1847-1851.

11. Kumar, N. N. B.; Chakravarty, M.; Kumar, N. S.; Sajna, K. V.; Kumara Swamy, K. C. *J. Chem. Sci.*, **2009**, *121*, 23-36 and references cited therein.

12. Morita, I.; Chokai, S.; Tsuda, M.; Kise, M.; Sugiyama, M. *Chem. Pharm. Bull.* **1988**, *36*, 1135

13. (a) Guillemin, J. C.; Savignac, P.; Denis, J. M. *Inorg. Chem.* **1991**, *30*, 2170 and references cited therein. (b) Sajna, K. V. *Cycloaddition/ Cyclization Reactions of Allenylphosphonates/ Related Allenes and Palladium-Catalyzed Diarylation of Alkynes*, PhD thesis, University of Hyderabad, 2011.

14. Boyes, A. L.; Wild, M. *Tetrahedron Lett*. **1998**, *39*, 6725.

15. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. *Purification of Laboratory Chemicals*; Pergamon: Oxford UK 1986.

16. Kumara Swamy, K. C.; Kumaraswamy, S.; Senthil Kumar, K.; Muthiah, C. *Tetrahedron Lett.* **2005**, *46*, 3347-3351.

17. Structure solution and refinement: Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Göttingen, Germany, **1996**. (b) Sheldrick, G. M., SHELX-97- *A program for crystal structure solution and refinement*, University of Göttingen, Germany, **1997**. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10.

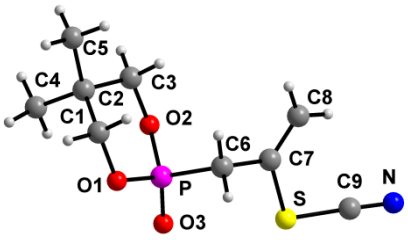


Figure 1. Molecular structure of compound **6a**. Selected bond lengths [Å] with esd's in parentheses: C(6)-P 1.789(3), C(6)-C(7) 1.485(4), C(7)-C(8) 1.311(4), C(7)-S 1.783(3), C(9)-S 1.664(4), C(9)-N 1.143(4). Bond angle (^{o}) for S-C(9)-N 177.5(4).

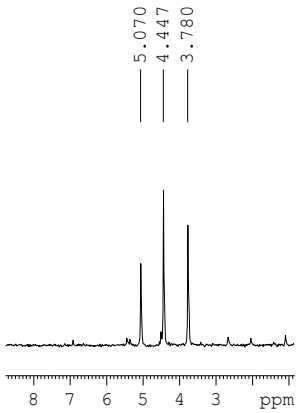
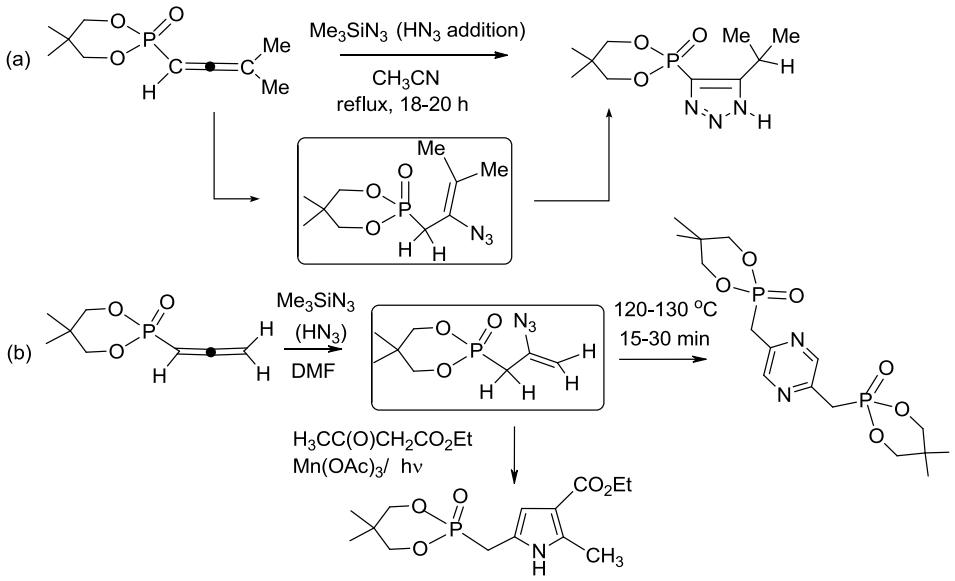
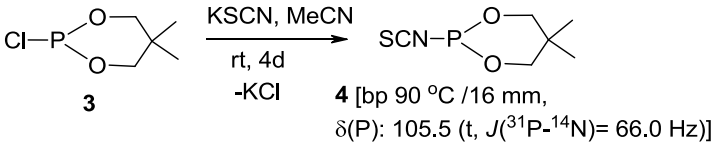


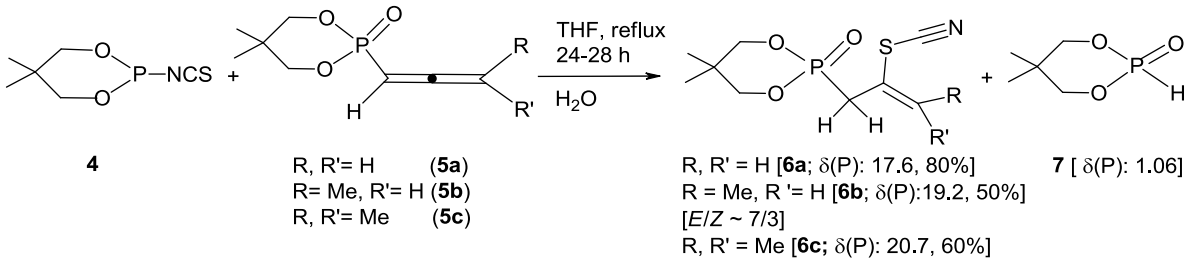
Figure 2. ^{31}P NMR spectrum for the reaction mixture resulting from the addition of $(COCl)_2/AgNO_3$ to allene **13**.



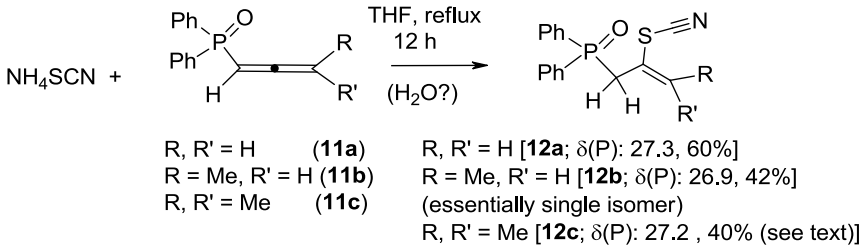
Scheme 1 Reactivity of vinyl azidophosphonates derived from allenylphosphonates.



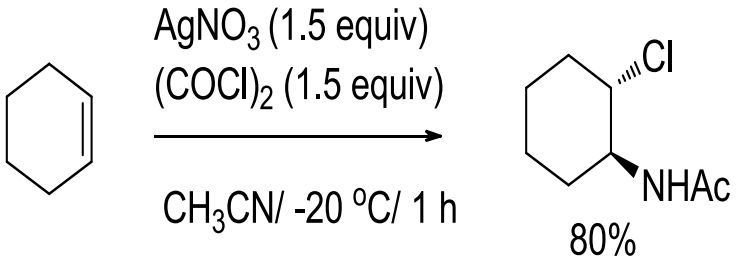
Scheme 2 Synthesis of the isothiocyanato compound **4**



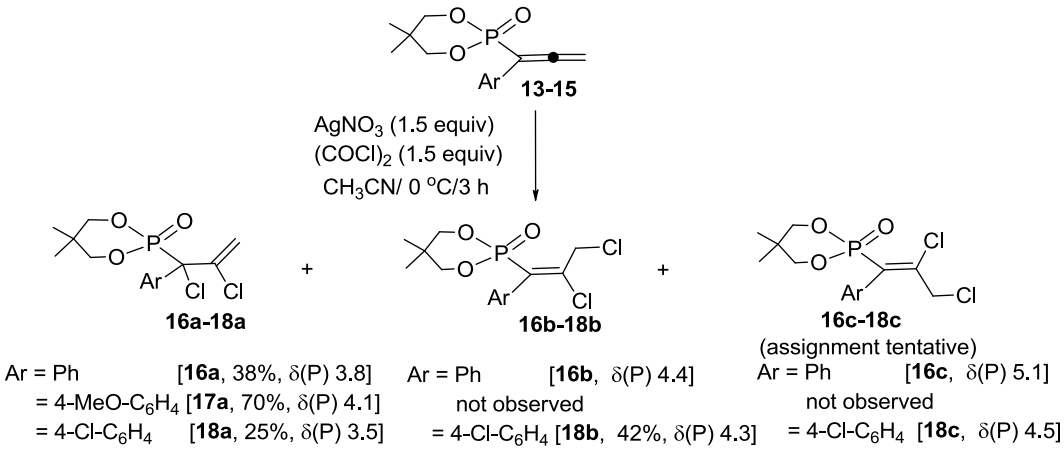
Scheme 3 Synthesis of the thiocyanato compounds **6a-6c**



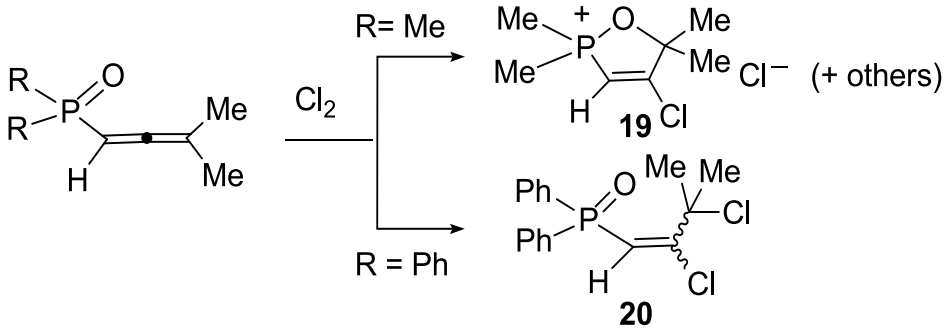
Scheme 4 Synthesis of the thiocyanato compounds **12a-12c** via NH_4SCN and allenes **11a-c**



Scheme 5 Amidochlorination reaction of cyclohexene using $AgNO_3/(COCl)_2$



Scheme 6 Vicinal chlorination of allenylphosphonates using $AgNO_3/(COCl)_2$



Scheme 7 Selected literature reports on chlorination of allenylphosphine oxides

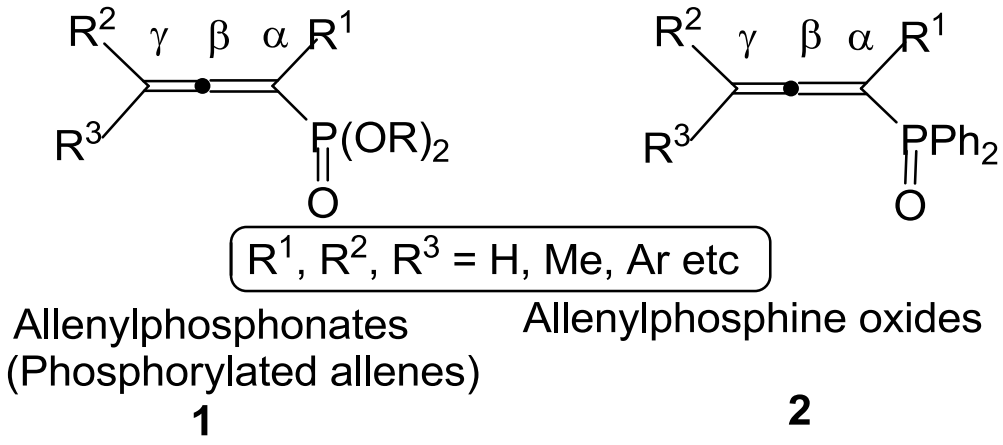


Chart 1 Phosphorus based allenes **1-2**