New reactions of allenes, alkynes, ynamides, enynones and isothiocyanates

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Abstract. This perspective article is related to transformations (both catalytic and non-catalytic) involving allenes, alkynes/enynones/ynamides and isothiocyanates. Part of the work from the author's group has been reviewed along with some new reactions of (i) allenylphosphonate/allenylphosphine oxide and (ii) a P(III) isothiocyanate. Thus, the allenylphosphine oxide $\text{Ph}_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{C}=\text{CH}_2$ undergoes base (DBU) catalyzed addition to the β -ketophosphonate $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ at 90°C to afford the addition product $\text{Ph}_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\text{CH}[\text{C}(\text{O})\text{Me}][\text{P}(\text{O})(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})]$. In an analogous reaction, with DBU as the base at 140°C , isomeric vinylphosphine oxides (*Z*)- $\text{Ph}_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\text{CH}_2[\text{C}(\text{O})\text{Me}]$ and (*E*)- $\text{Ph}_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{Me})\text{CH}_2[\text{C}(\text{O})\text{Me}]$ were isolated. The *E*-isomer has been characterized by single crystal X-ray structure determination. In another set of studies, the reaction of P(III) isothiocyanate $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{NCS})$ with *N*-(2-bromomethyl)sulfonamide afforded an unusual product with the formula $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{O})\text{SCH}_2\text{CH}_2\text{NHS}(\text{O})_2-(\text{C}_6\text{H}_4-4-\text{Me})$ as shown by X-ray structure determination. This result is different from that obtained in the recently reported analogous reaction using phenyl isothiocyanate.

Keywords. Allene; allenylphosphine oxide; enynone; ynamide; P(III) isothiocyanate; X-ray structure.

1. Introduction

The enormous reactivity of organic substrates possessing *sp*-hybridized carbon, as in alkynes or allenes, has led to numerous synthetic methodologies.¹ In many reactions involving alkynes, allenic intermediates have been proposed or isolated and in some cases this feature has been utilized as a synthetic route to specific class of allenes (cf. Figure 1).^{1,2} Ynamides are also a special type of alkynes in which the reactivity may depend on the ketenimium species that are analogous to allenes.³ Another class of alkynes, the enynones/enynals, also have reactivity that are typical of normal alkynes but can show additional features because of the conjugated system.⁴ Perhaps more interesting correlation is to a system like that of isothiocyanates (or isocyanates/ CO_2/CS_2) that have a

central carbon that is *sp*-hybridized and amenable for nucleophilic attack.⁵ The unsaturated systems such as these are also useful in diverse catalytic transformations. Some aspects of reactions of these substrates from our research group will be highlighted in this short paper.

2. Experimental

Solvents were dried according to known methods as appropriate.⁶ ^1H , ^{13}C and ^{31}P NMR spectra (^1H -400 MHz or 500 MHz, ^{13}C -100 MHz or 125 MHz and ^{31}P -162 MHz) were recorded using a 400 MHz or 500 MHz spectrometer in CDCl_3 (unless stated otherwise) with shifts referenced to SiMe_4 ($\delta = 0$). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. High-resolution mass spectra (HR-MS) were performed using a BRUKER-MAXIS mass spectrometer with ESI-QTOF-II method.

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Figure 1. Some reactive species possessing central *sp*-hybridized carbon.

2.1 Synthesis of (*E*)-3,5-bis(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-4-methyl-5-phenylpent-4-en-2-one (**21**) (Scheme 6)

To an oven dried Schlenk tube, ketone **19** (0.35 g, 1.70 mmol), allenylphosphonate **20** (0.45 g, 1.70 mmol), K_2CO_3 (0.047 g, 0.341 mmol) and dry DMSO (5 mL) were added. The contents were sealed under nitrogen atmosphere and stirred at 90 °C (oil bath temperature) for 8 h. After completion of the reaction as monitored by TLC, the crude reaction mixture was cooled to 25 °C, diluted with ethyl acetate (20 mL) and washed with water. The organic layer was washed with brine solution, dried over anhyd. Na_2SO_4 and concentrated under vacuum. The residue was purified by using silica gel column chromatography with hexane-ethyl acetate (3:7) as the eluent to afford (*E*)-3,5-bis(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-4-methyl-5-phenylpent-4-en-2-one (**21**). Compound **21**: Yield: 0.309 g (68%); gummy liquid; IR (KBr): 3057, 2973, 2886, 1809, 1715, 1605, 1472, 1373, 1283, 1071, 916, 829, 735, 704, 635 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 3H), 7.19 (br m, 2H), 6.38 (d, J = 24.8 Hz, 1H), 4.62 (d, J = 11.2 Hz, 1H), 4.53 (d, J = 11.2 Hz, 1H), 3.97–3.82 (m, 4H), 3.62 (t, J = 12.0 Hz, 1H), 3.32 (t, J = 13.4 Hz, 1H), 2.41 (s, 3H), 1.91 (s, 3H), 1.30 (s, 3H), 0.95 (s, 6H), 0.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 151.6 (J = 10.4, 5.5 Hz), 136.6 (J = 9.0 Hz), 130.8 (J = 164.9, 12.1 Hz, P–C), 130.0, 129.8, 128.6, 127.8, 76.1 (J = 6.4 Hz), 75.8 (J = 6.1 Hz), 57.4 (J = 6.3 Hz), 56.2 (J = 6.3 Hz), 56.8 (J = 117.5, 6.3 Hz, P–C), 32.6 (J = 7.2 Hz), 32.3 (J = 6.6 Hz), 30.3, 22.1, 21.7, 21.2 (J = 16.4 Hz), 20.7, 20.4; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 11.7 (J = 6.0 Hz), 10.7 (J = 5.8 Hz); LC/MS: m/z 471 [M^+ +H]; Anal. Calcd. $C_{22}H_{32}O_7P_2$: C, 56.17; H, 6.86%; Found: C, 56.31, H, 6.81%. HRMS (ESI): Calcd. for $C_{22}H_{33}O_7P_2[M^+$ +H]: m/z 471.1702. Found: 471.1703.

2.2 Synthesis of (*E*)-3-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-5-(diphenylphosphoryl)-4-methyl-5-phenylpent-4-en-2-one (**23**) (Scheme 6)

To an oven dried Schlenk tube, ketone **19** (0.17 g, 0.80 mmol), allene **22** (0.25 g, 0.80 mmol) and DBU (0.025 g, 0.16 mmol) in dry DMSO (5 mL) were added. The contents were sealed under nitrogen atmosphere and stirred at 90 °C (oil bath temperature) for 8 h. The work up and isolation of the compound were similar to that given above using hexane-ethyl acetate (7:3) as the eluent to afford (*E*)-3-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-5-(diphenylphosphoryl)-4-methyl-5-phenylpent-4-en-2-one (**23**). Compound **23**: Yield: 0.250 g (60%); gummy liquid ~95% purity; IR (KBr): 3063, 2973, 2926, 1717, 1481, 1420, 1370, 1285, 1117, 1057, 1013, 791, 756, 725, 700 cm^{-1} ; 1H NMR (400MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.48–7.32 (m, 4H), 7.26–7.21 (m, 4H), 7.14–7.01 (m, 7H), 6.99–6.79 (m, 3H), 6.39 (d, J = 6.8 Hz, 1H), 4.88–4.82 (m, 2H), 4.02–3.84 (m, 2H), 2.14 (s, 3H), 1.92 (s, 3H), 1.19 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 200.0, 151.2, 137.5 (J = 11.6 Hz), 133.3, 132.2, 131.9 (J = 10.4 Hz), 131.6 (J = 10.4 Hz), 131.5, 130.6 (J = 106.5 Hz, P–C), 130.3, 129.4, 128.9, 128.8, 128.4, 128.2, 127.7, 127.6, 127.1, 122.8, 93.9, 82.0, 77.2 (d, J = 8.7 Hz), 65.5, 56.7 (J = 109.1 Hz, P–C), 32.8 (J = 7.2 Hz), 31.5, 30.4, 29.7, 22.3 (J = 11.4 Hz), 22.2, 20.4., $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 31.7 (d, J = 4.1 Hz), 12.3 (d, J = 4.1 Hz); LC/MS m/z 471 [M^+ +H]. HRMS (ESI): Calcd. for $C_{29}H_{33}O_5P_2$ [M^+ +H]: m/z 523.1804. Found: 523.1804

2.3 Synthesis of (*Z*)-5-(diphenylphosphoryl)-4-methyl-5-phenylpent-4-en-2-one (**24**) and (*E*)-5-(diphenylphosphoryl)-4-methyl-5-phenylpent-4-en-2-one (**25**) (Scheme 6)

To an oven dried Schlenk tube, allene **22** (0.50 g, 1.58 mmol), ethyl acetoacetate (0.31 g, 2.37 mmol), DBU (0.048 g, 0.31 mmol), DMSO (5 mL) were added. The contents were sealed under nitrogen atmosphere and heated with stirring at 140 °C (oil bath temperature) for 6 h. The work up was similar to above and the compounds (*Z*)-5-(diphenylphosphoryl)-4-methyl-5-phenylpent-4-en-2-one (**24**; higher R_f) and (*E*)-5-(diphenylphosphoryl)-4-methyl-5-phenylpent-4-en-2-one (**25**; lower R_f) were isolated using hexane-ethyl acetate (4:6) as the eluent. Compound **24**: Yield: 0.172 g (29%, purity >95%); gummy liquid; IR (KBr): 3057, 2922, 1715, 1678, 1609, 1487, 1437, 1358, 1316, 1173, 1115, 1026, 754 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 5H), 7.40–7.38 (m, 2H), 7.32–7.27 (m, 5H), 7.04–7.02 (m, 3H), 6.79–6.77 (m, 2H), 4.18 (s, 2H), 2.04 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 151.8 (J = 6.1 Hz), 138.2 (J = 11.2 Hz), 132.8 (J = 103.0 Hz, P–C), 131.7, 131.6, 131.3, 131.2, 131.0, 130.1, 130.0, 128.5, 128.1, 127.9, 126.7, 50.1 (J = 6.8 Hz), 30.1, 24.2 (J = 11.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 28.9; LC/MS m/z 375

[M⁺ + H]. HRMS (ESI): Calcd. for C₂₄H₂₄O₂P [M⁺ + H]: *m/z* 375.1515. Found: 375.1515.

Compound **25**: Yield: 0.207 g (35%); white solid, M.p.: 172–176 °C; IR (KBr): 3048, 2924, 1715, 1678, 1609, 1478, 1437, 1358, 1315, 1173, 1115, 1026, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.66–7.61 (m, 4H), 7.40–7.38 (m, 2H), 7.32–7.27 (m, 4H), 6.99–6.96 (m, 3H), 6.80 (d, *J* = 6.8 Hz, 2H), 3.19 (s, 2H), 2.25 (d, *J* = 2.8 Hz, 3H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 205.6, 151.0 (*J* = 7.8 Hz), 134.4, 133.4, 133.3 (*J* = 103.0 Hz, P-C), 132.0, 131.9, 131.3, 129.4, 128.2, 128.1, 126.9, 52.6 (*J* = 11.6 Hz), 30.3, 23.0 (*J* = 7.5 Hz); ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 29.2; LC/MS *m/z* 375 [M⁺ + H]; Anal. Calcd. C₂₄H₂₃O₂P: C, 76.99; H, 6.19%; Found: C, 77.1, H, 6.15%. HRMS (ESI): Calcd. for C₂₄H₂₄O₂P [M⁺ + H]: *m/z* 375.1515. Found: 375.1517.

2.4 Synthesis of *N*-(2-((5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)thio)ethyl)-4-methylbenzene sulfonamide (**48**) (Scheme 13)

N-(2-Bromoethyl) sulfonamide **45** (0.36 mmol) and 3-((isothiocyanato(methyl)phosphino)oxy)-2,2-dimethylpropan-1-ol **47** (0.54 mmol) were used. Yield 0.118 g (86%, white solid); M.p.: 136–138 °C; IR (KBr) *v*_{max} 3175, 2974, 1324, 1262, 1155, 1092, 1050, 1000, 835, 782, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.69 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.19 (br, 1H), 4.08 (d, *J* = 12.0 Hz, 2H), 3.90–3.83 (m, 2H), 3.20–3.18 (m, 2H), 2.95–2.92 (m, 2H), 2.36 (s, 3H), 1.21 (s, 3H), 0.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 137.1, 129.7, 127.0, 78.1 (*J* = 5.5 Hz), 43.6 (*J* = 2.1 Hz), 32.4 (*J* = 6.0 Hz), 29.4, 21.8, 21.4, 20.2; ³¹P NMR (162 MHz, CDCl₃) δ 20.74; HRMS (ESI) calcd. for C₁₄H₂₂NO₅PS₂Na(M⁺ + Na) 402.0575, found: 402.0575. This compound was crystallized from dichloromethane/ethyl acetate (2:1) mixture at 25 °C.

2.5 X-ray structural analysis of compounds **25** and **48**

Single crystal X-ray data for compounds **25** and **48** were collected on a Bruker AXS-SMART or OXFORD diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full-matrix least squares method using standard procedures.⁷

Compound **25**: C₂₄H₂₃O₂P, *M* = 374.39, monoclinic, space group *P*2₁/n, *a* = 11.9638(7) Å, *b* = 10.6625(5) Å, *c* = 16.0875(8) Å, β = 93.956(5)°, *V* = 2047.30(17) Å³, *Z* = 4, μ = 0.150 mm⁻¹, data/restraints/parameters 3598/0/246, *R* indices (*I* > 2σ(*I*)) *R*1 = 0.0454, *wR*2 (all data) = 0.1145. CCDC no. 1834021.

Compound **48**: C₁₄H₂₂NO₅PS₂, *M* = 379.42, triclinic, space group *P*-1, *a* = 6.8296(8) Å, *b* = 7.4875(8) Å, *c* = 18.4067(19) Å, α = 80.149(5), β = 81.744(5), γ = 82.580(4), *V* = 912.47(17) Å³, *Z* = 2, μ = 0.440 mm⁻¹, data/restraints/parameters 3205/4/214, *R* indices (*I* > 2σ(*I*)) *R*1 = 0.1064, *wR*2 (all data) = 0.2825. The quality of data

was only moderate, but the refinement could be satisfactorily done. CCDC no. 1575674.

3. Results and Discussion

3.1 Reactivity of allenylphosphonates/allenylphosphine oxides

Selected reactions of allenylphosphonates/allenylphosphine oxides reported from our laboratory are shown in Scheme 1.⁸ Many of these have been summarized in a recent article.^{8a} While performing these reactions we were also curious to see whether some intermediates can be isolated. For example, in the reaction shown in Scheme 2a, two equivalents of the thiophosphite (OCH₂CMe₂CH₂O)P(S)H (**2**) can be added (cf. compound **5**) on to the allene **1** in the presence of Pd(PPh₃)₄, but in a blank reaction in the absence of allene, we could isolate the [Pd] species **6** (Scheme 2b). Interestingly, this compound **6** was also very effective in catalyzing the same phosphorylation reaction.^{8b}

In another study, we were investigating the phosphorylation reactions of allenylphosphonates and Baylis-Hillman adducts using tetrabutylammonium fluoride [(*n*-Bu)₄NF] as the catalyst in ionic liquid [bmim]⁺[PF₆]⁻ as the medium (Scheme 3).⁹ It is important to note that pentacoordinate phosphorus intermediates are proposed in numerous reactions involving tetracoordinate phosphorus. However, they have been rarely been identified spectroscopically. In the present case, we have been able to elegantly identify such an intermediate [Scheme 3b; case (ii)] by the combined use of ³¹P, ¹H and ¹⁹F NMR spectroscopy wherein the values of ¹*J*PF [959.5 Hz], ¹*J*PH [652.4 Hz] and ²*J*FH [129.4 Hz] could be easily discerned.⁹ The ¹H NMR and ¹³C NMR spectra were also consistent with the phosphocin ring being intact.

In another interesting reaction of allenes wherein both phosphine and gold catalysis is involved, we chose an allenolate **10**. Thus, in a one-pot reaction, the allenolate **10** reacted with the enynal **11** to afford trisubstituted benzofuran **13** via cyclopentene intermediate **12** (Scheme 4).¹⁰ For the first step in the formation of the cyclopentenones **12**, initial attack of the phosphine on the allenolate **10** can be envisaged. However, to date, the exact species of type **14** has not been characterized. The closest that we have been able to isolate and structurally characterize are the compounds **16'** and **16''** using the *Inorganic ring* system [(*t*-BuNH)P[N(*t*-Bu)]₂P(NH-*t*-Bu)] (**15**).¹¹ Thus attack of the trivalent phosphorus on the central *sp*-hybridized β-carbon of the allene affords **16** which

Scheme 1. Cyclization/cycloaddition reactions of allenylphosphonates/allenylphosphine oxides. Conditions: (i) K_3PO_4 (0.5 equiv.), THF, 80 °C, 12 h/ NaOH (2 equiv.), EtOH/H₂O (4:1), 80 °C, 8 h;^{8a} (ii) K_2CO_3 (20 mol%), DMSO, 90 °C, 4 h;^{8e} (iii) K_3PO_4 (20 mol%), DMSO, 120 °C, 8–12 h;^{8a} (iv) Propargylic alcohols, $Zn(OTf)_2$ (10 mol%), Et₃N (20 mol%), toluene, 100 °C, 8 h;^{8c} (v) Et₂NH, CH₃CN, rt (25 °C), 8 h;^{8a} (vi) K_2CO_3 (20 mol%), DMSO, 90 °C, 24 h;^{8e} (vii) $ZrCl_4$ (0.5 mol equiv.), MeOH, reflux, 2–3 h;^{8a} (viii) Me_3SiN_3 , CH₃CN, reflux, 18–20 h;^{8f} (ix) Me_3SiN_3 , DMF/CH₃C(O)CH₂CO₂Et, Mn(OAc)₃, MeOH, rt;^{8a} (x) K_2CO_3 (20 mol%), PEG-400, 90 °C, 4 h.^{8d}

Scheme 2. [Pd]-catalyzed thiophosponylation of allenylphosphonate **1** and isolation of the catalytically active intermediate **6**.

then rearranges to **16'**/**16''**. Conversion of cyclopentene **12** to the benzofuran **13** is also complex but is assumed to involve the [Au]-intermediates **17**/**17'** (Scheme 5).

Sterically unhindered allenylphosphonates are susceptible to attack by water and thus $(OCH_2CMe_2CH_2O)P(O)CH=C=CH_2$ **18** can be converted to the β -ketophos-

Scheme 3. The $[(n\text{-Bu})_4\text{NF}]$ mediated/catalyzed addition of a phosphite to allenylphosphonate showing the pentacoordinate phosphorus species.

Scheme 4. One pot PPh_3 and $[\text{Au}]$ -catalyzed reaction of allenolate with enynal for the formation of multiply substituted benzofuran.

Scheme 5. (a) Possible intermediates in the phosphine catalyzed reaction of allenolate; (b) Isolation of intermediate-type species using cyclodiphosphazane and; (c) Two plausible intermediates in the $[\text{Au}]$ catalyzed reaction of alkyne substituted cyclopentenes.

Scheme 6. (a) Formation of β -ketophosphonate **19** from allenylphosphonate **18**; (b)–(c) reactions of allenylphosphonate **20** and allenylphosphine oxide **22** with β -ketophosphonate **19** to afford **23**; (d) reaction of allenylphosphine oxide **22** with ethyl acetoacetate to afford **24–25**.

phosphate $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ (**19**)¹² in the presence of a base. Since compound **19** can take part in Horner-Wadsworth reaction, we envisaged that the anion thus obtained should act as a nucleophile towards the central *sp*-hybridized carbon of the allenylphosphonate of type **20**. Indeed this reaction did occur and we could readily isolate the bisphosphonate **21**. A similar reaction occurred using the allenylphosphine oxide **22** and phosphonate-phosphine oxide **23** was obtained in decent yields. In the latter case though, we used DBU as the base. Interestingly, in the reaction of allenylphosphine oxide **22** with ethyl acetoacetate, we obtained a different set of products, the isomeric **24–25** in which the ester moiety was removed probably *via* adventitious moisture present in the system. The X-ray structure of the *E*-isomer, **25** has been determined (Figure 2). It is possible that the olefinic double bond may shift itself to give enone isomers in these cases. Indeed in the reaction of **22** with ethyl acetoacetate in the presence of K_2CO_3 or DABCO such isomers appear to form,¹³ but these reactions need to be studied further in order to get insight into the mechanistic details as well as utility.

3.2 Alkyne enynone/enynal/dynamide reactivity

As mentioned above (cf. Figure 1) both alkyne and allene have a reactive *sp*-hybridized carbon. One of the

Figure 2. Molecular structure of compound **25** showing the *E*-configuration. Only selected hydrogen atoms are shown. Selected bond distances (Å) with esds: P1–O1 1.486(1), P1–C7 1.796(2), P1–C1 1.809(2), P1–C13 1.821(2), C13–C20 1.341(3), C20–C22 1.500(3), C20–C21 1.510(3). CCDC No. 1834021.

reactions that we investigated is the double arylation of alkynes.¹⁴ Analogous reactions are generally carried out in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ in a nonaqueous solvent.¹⁵ Interestingly, we could effect this reaction of the alkyne **26** on water within a very short time using the palladium catalyst **6** alluded to before (cf. Scheme 7),

Scheme 7. Double arylation of alkyne **26** using our catalyst **6** on water to afford **27**.

Scheme 9. [Ru]-catalyzed alkyne insertion onto purine base appended aniline *via* C-H activation.

giving rise to the double arylated product **27**.¹⁴ The reaction could be readily monitored by ³¹P NMR spectroscopy which suggested that catalyst **6** is more efficient than the traditional [Pd(PPh₃)₄] and readily afforded clean products.

In a significant number of reactions involving alkyne insertion, the ruthenium catalyst [RuCl₂(*p*-cymene)]₂ is used.¹⁶ The substrate generally has a directing group (e.g., 8-aminoquinoline). In reactions such as these, it is generally assumed that both the chlorines of [RuCl₂(*p*-cymene)]₂ are replaced under catalytic conditions. However, for the annulation reaction shown in Scheme 8, we found that only one of the chlorines on the catalyst/pre-catalyst [RuCl₂(*p*-cymene)]₂ gets replaced in the absence of the substrate **28** to afford the complex [RuCl(OAc)(*p*-cymene)] (**30**). What is more interesting is that this intermediate **30** reacts with *N*-quinolin-8-ylbenzamide **28** to give the ruthenium complex **31** that can also act as a catalyst for the alkyne insertion.¹⁷ Thus,

Scheme 10. Gold-catalyzed the formation of triazine fused furans; the possible intermediates are also shown.

this study suggested that there may be other (previously not formulated) intermediates for this alkyne insertion reaction.

Scheme 8. (a) Alkyne insertion using the ruthenium catalyst/precatalyst [RuCl₂(*p*-cymene)]₂ and (b) isolation of an intermediate type ruthenium complex **31**.

Scheme 11. (a) Sulfur/selenium insertion reaction of ynamides and; (b) *E*-selective hydrogenation of ynamides using ethanol as the hydrogenating agent.

In another alkyne insertion reaction on the substrate **32** leading to the annulated product **33** shown in Scheme 9, we have used purine as the directing group.¹⁸ In a manner similar to that shown in Scheme 8, we were able to isolate the ruthenium complex **34**. Such an observation suggests that in these reactions $[RuCl_2(p\text{-cymene})]_2$ acts only as a pre-catalyst.

Enynones/enynals have double bonds, generally in conjugation with the alkyne moiety. This structural feature may impart new type of reactivity for such a substrate. One such example reported from our group using

the alkynophilic $[Au]$ catalysts is shown in Scheme 10.¹⁹ Here, the reaction of azide with the enynone/enynal under gold catalysis leads to the formation of a 6-membered triazine ring compound, rather than the familiar click reaction in which a triazole is obtained. The main condition for this to happen is that the group R^1 has to be aromatic. Several $[Au]$ -intermediates are involved in this process; three of them are shown in the scheme.

Ynamides belong to a special type of alkynes in which the reactivity of the two *sp*-hybridized carbon atoms of the alkyne exhibit vastly different reactivity.³ One example in which we could insert elemental sulfur or selenium directly into the ring system *via* copper catalysis is demonstrated in Scheme 11a.²⁰ Here, the initial reaction of CuI with the iodo-substituted ynamide is assumed to lead to an intermediate in which the copper is connected to the arene [cf. Scheme 11a). The sulfur $[S_n]^{2-}$ (or similar selenide) anion is produced from sulfur in the presence of the base K_2CO_3 and water. Perhaps a more interesting reaction of the ynamide is catalytic hydrogenation using ethanol as the hydrogenating agent under palladium catalysis. An example of this is shown in Scheme 11b.²¹ Here, the *E*-enamide is formed preferentially.

3.3 Isothiocyanate reactivity

Carbon disulfide ($S=C=S$), as well as aryl isothiocyanates $ArN=C=S$, have a central *sp*-hybridized carbon which is susceptible to nucleophilic attack.⁵ In this sense, this system is analogous to the allene system described above (cf. Figure 1). We have been interested

Scheme 12. Base-mediated reaction of cumulenes ($CS_2/PhNCS$) with epoxy sulfonamides.

Scheme 13. (a) Reaction of aryl isothiocyanate **44** with bromoethylsulfonamide **45** to afford **46**; (b) Unusual reaction of bromoethyl-sulfonamide with P(III) isothiocyanate **47** to afford **48**.

Figure 3. Molecular structure of compound **48**. The data quality was only moderate in this case. Selected bond lengths [Å] with esds in parentheses: N1–C7 1.404(8), C8–C7 1.398(9), S2–C8 1.777(7), P1–S2 2.052(4), P1–O3 1.427(7), N1–H1 0.751(11), S1–N1 1.583(10). CCDC no. 1575674.

in extending the chemistry of allenes to include carbon disulfide or isothiocyanates/isocyanates. An example from a recent report is shown in Scheme 12.²² In this case, a nucleophile is generated by the removal of NH proton from **41** in the presence of the base; this nucleophile attacks the *sp*-hybridized carbon center of carbon disulfide or isothiocyanate/isocyanate in a manner analogous to that with central carbon of allenes. Subsequent cyclization/epoxide ring opening and the addition of proton leads to the final products of types **42–43**.

In our earlier work on P(III) compounds, we had noted that P(III) azides react in a manner different from organic azides.^{23a–b} Hence, to know whether a P(III) isothiocyanate **47** will react in a manner similar to the traditional organic isothiocyanate **44** (Scheme 13a, cf. product **46**), we treated the precursor **47** with the bromoethyl-sulfonamide **45**. This reaction did take place, but in a direction entirely different from the above, leading to the product **48**. In this case, the formation of new P–S and C–S bonds has taken place in addition to the oxidation at the phosphorus center. IR,

NMR (¹H and ¹³C) and HRMS data are consistent with the structure shown below (Scheme 13b). The structure of compound **48** was also confirmed by X-ray crystallography (Figure 3). More investigations, though, are needed to rationalize this observation.

4. Conclusions

Recent work on the reactions of allenylphosphonates/allenylphosphine oxides, alkynes, enynones, ynamides and isothiocyanates has been summarized. In a new set of reactions, it is shown that allenylphosphonates/allenylphosphine oxides undergo addition reactions with β -ketophosphonate to lead to products in which the nucleophilic attack at the central *sp*-hybridized carbon of the allene is involved. In a slightly different pathway, allenylphosphine oxide (e.g., **22**) reacted with ethyl acetoacetate to afford isomeric vinylphosphine oxides with the elimination of the ester moiety in the presence of adventitious moisture. It is also shown that the reactivity of a P(III) isothiocyanate is different from the reaction of traditional organic isothiocyanates.

Supplementary Information (SI)

Spectroscopic data for the new compounds reported here will be available from the authors. Crystallographic data for **25** and **48** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1834021 and 1575674. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk]. Supplementary information is available at www.ias.ac.in/chemsci.

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 13. Using K_2CO_3 (2 equiv.) at $140^\circ C$ for 6 h and with similar molar quantities of the reactants product **A** (purity >95%) was isolated. Use of DABCO (2 equiv.) at $85^\circ C$ for 20 h, however, led to the isolation of the second isomer, product **B**. Tentatively assigned structures are shown below. Product **A**: M.p. $166 - 170^\circ C$; IR (KBr): 3057, 2928, 1688, 1611, 1493, 1437, 1356, 1263, 1179, 1117, 1073, 723, 696 cm^{-1} ; 1H NMR(400MHz, $CDCl_3$) δ 7.83–7.80 (m, 2H), 7.54–7.20 (m, 13H), 6.70 (s, 1H), 4.18 (d, $J = 8.2\text{ Hz}$, 1H), 2.13 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H). ^{13}C NMR(100MHz, $CDCl_3$) δ 198.7, 151.6 ($J = 5.1\text{ Hz}$), 134.1 ($J = 5.0\text{ Hz}$), 132.8, 132.5, 131.9, 131.8, 131.6, 131.5, 131.2, 131.1, 131.0, 130.1, 128.7, 128.6, 128.5, 128.3, 128.23, 128.18, 128.1, 127.6, 57.1 ($J = 64.7\text{ Hz}$), 32.0, 20.15, 20.09, ^{31}P NMR(162MHz, $CDCl_3$) δ 30.3; LC/MS m/z 375 [$M^+ + H$]. Product **B**: gummy liquid; IR (KBr): 3052, 2932, 1677, 1595, 1490, 1436, 1353, 1178, 1118, 1023, 696 cm^{-1} ; 1H NMR(400MHz, $CDCl_3$) δ 7.87–7.71 (m, 6H), 7.44–7.14 (m, 10H), 6.95 (d, $J = 22.0\text{ Hz}$, 1H), 5.91 (s, 1H), 2.10 (s, 3H), 1.92 (s, 3H), 2.04 (s, 3H). ^{13}C NMR(100MHz, $CDCl_3$) δ 199.1, 153.8 ($J = 6.0\text{ Hz}$), 135.3 ($J = 5.0\text{ Hz}$), 132.7, 132.3, 131.7, 131.5, 131.3, 131.2, 131.15, 131.09, 131.01, 130.7, 130.6, 128.52, 128.49, 128.4, 128.2, 128.1, 127.3, 125.8, 125.7, 46.5 ($J = 65.0\text{ Hz}$), 32.1, 23.5 ($J = 3.0\text{ Hz}$); ^{31}P NMR(162MHz, $CDCl_3$) δ 31.6; LC/MS m/z 375 [$M^+ + H$].
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