DOI: 10.1002/ejoc.200800490

Allenylphosphonates − Useful Precursors of Pyrazoles and 1,2,3-Triazoles

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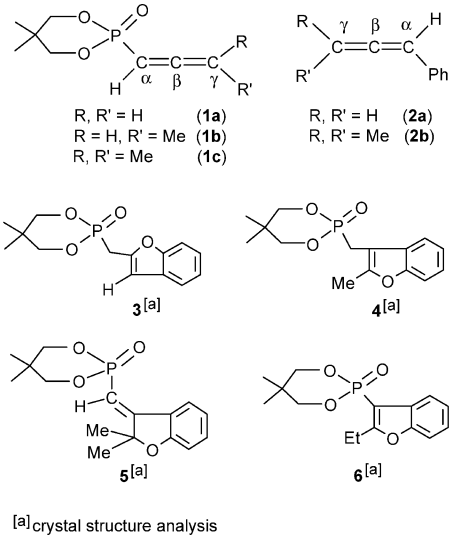
Keywords: Allenes / Phosphonates / Heterocycles / Pyrazoles / Triazoles

The synthesis of new pyrazoles and triazoles, with or without phosphorus substituents, from allenylphosphonates is described. Thus, Ph_3P-promoted reactions of the allenylphosphonates $(OCH_2CMe_2CH_2O)P(O)CH=C=CRR'$ [R = H, R′ = Me (**1b**), R = R′ = Me (**1c**)] with DIAD/DEAD lead to phosphonopyrazoles by utilizing the $–CO_2R$ functionality of DIAD/DEAD for cyclization. The products derived from allenylphosphonates with an α-phenyl group undergo an unusual but facile P–C bond cleavage to form tetrasubstituted pyrazoles. In the second type of reaction, Me_3SiN_3 reacts with the allenylphosphonates to form phosphono-1,2,3-triazoles in CH_3CN at reflux, whereas (β-azidoallyl)phosphonates were obtained in high yields at room temperature. These latter compounds undergo cycloaddition with activated acetylenes to afford multisubstituted 1,2,3-triazoles. They were subsequently transformed into diverse *N*-substituted 1,2,3-triazoles through the Horner–Wadsworth–Emmons reaction. The structures of the key compounds were established by X-ray crystallography.

Introduction

Allenes (or 1,2-dienes) are versatile precursors of a variety of industrially and biologically significant molecules.[1,2] Allenylphosphonates (phosphorylated allenes) **1a**–**c** can also be used as important building blocks in organic chemistry.[3] Organophosphonates themselves are important molecules in chemistry and biochemistry.[4,5] As phosphorus can impart a different electronic constraint on the intermediates compared with an aryl carbon of aryl-substituted allenes, the stereochemistry of the products obtained by using allenylphosphonates and other substituted allenes (e.g., **2a**,**b**) may be the result of different pathways. As an example, we have shown recently that in the palladium-catalyzed reactions of **1a**–**c** with iodophenol, a variety of benzofurans (e.g., **3**–**6**) can be obtained.[6,7] We have also shown by using **1a** and related allenes that in the nucleophilic addition of amines to allenylphosphonates, the stereochemistry of the β-aminophosphonate products depends upon the type of amine used (cf. compounds **7**–**11**).[8]

In the above context, we became interested in (i) the phosphane-promoted addition of dialkyl azodicarboxylates and (ii) the (non-catalyzed) addition of hydrazoic acid via trimethylsilyl azide. Whereas the former has the potential to afford phosphonopyrazoles, the latter could lead to phosphonotriazoles or -azirines. Pyrazoles find extensive use in the pharmaceutical industry,[9] but there are only limited number of routes available for their synthesis.[10] The



1,2,3-triazoles also have a wide range of applications in agrochemicals, corrosion inhibition, the dye industry and as pharmaceuticals.[11]

Recently, the phosphane-promoted addition of dialkyl azodicarboxylates $RO_2CN=NCO_2R$ [R = Et (DEAD) or *i*Pr (DIAD)] has been elegantly utilized to generate new pyrazole/pyrazoline derivatives (Scheme 1).[12,13] This addition reaction occurs via the Morrison–Brunn–Huisgen (MBH) intermediate $Ph_3P^+N(CO_2R)–N^––CO_2R$ (**12**),[14] which is also the critical component in the Mitsunobu reaction.[15,16] With the readily available and inexpensive allenylphosphonates in our hands,[6,17] we were curious to know whether phosphono-substituted pyrazoles could similarly be obtained or not. As regards the addition reaction with

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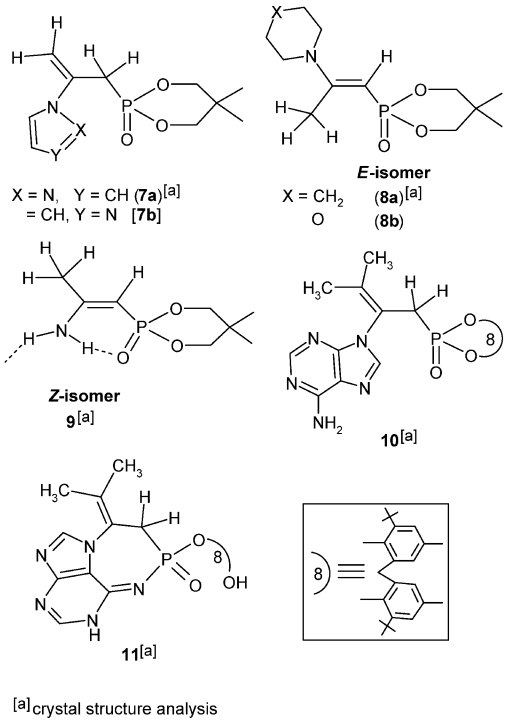
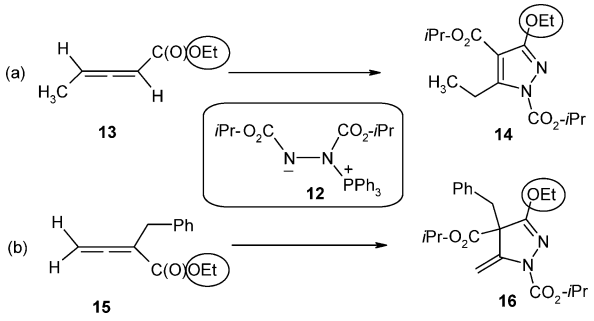
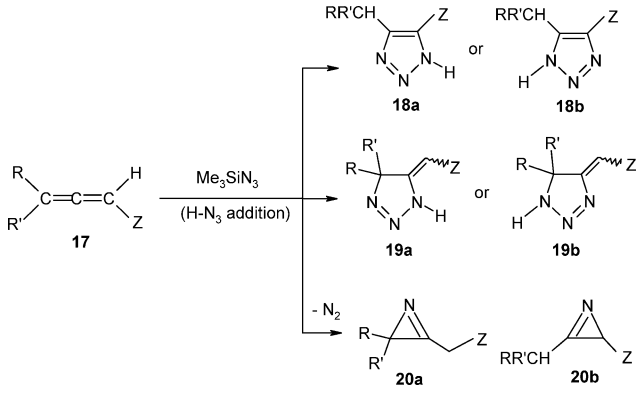


Me_3SiN_3, it was prompted by our desire to investigate the feasibility of triazole/dihydrotriazole (e.g., **18** and **19**) versus azirine (**20**) formation (Scheme 2). It should be emphasized here that Me_3SiN_3 was used as a source of HN_3 in several reactions.[18] In this paper we address the synthetic aspects



Scheme 1.



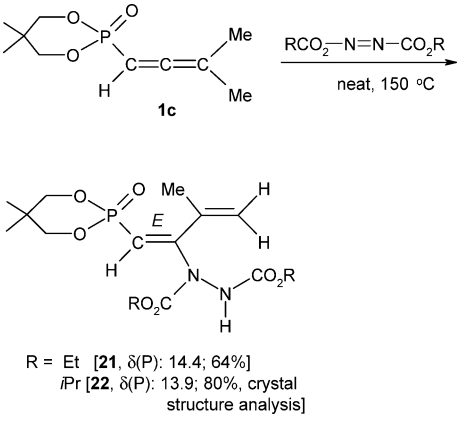
Scheme 2.

of these two systems, which primarily use inexpensive allenylphosphonates. A hitherto unreported unusual P–C bond-cleavage reaction is also highlighted.

Results and Discussion

Reaction of Allenylphosphonates with Dialkyl Azodicarboxylates

With DEAD/DIAD in the absence of triphenylphosphane, allene **1a** did not react. Allene **1b** gave a mixture and **1c** gave stable butadiene products **21** and **22** regio- and stereospecifically in ≥80% yield (based on ^{31}P NMR spectroscopy, Scheme 3). This feature appears to be general for $=CMe_2$ terminal allenes because we could isolate analogous butadienes **24** and **25** starting from the allene **23**.[6,19] The *E* stereochemistry was confirmed by X-ray crystallography in the case of **22** (Figure 1). Once formed, the butadienes did not cyclize to form the pyrazoles, even upon prolonged heating. Interestingly, the formation of similarly substituted hydrazine derivatives in the reaction of MBH betaine with ketones has been reported recently by Lee and co-workers.[13]



Scheme 3.

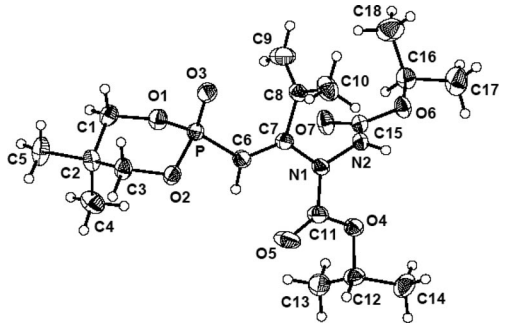
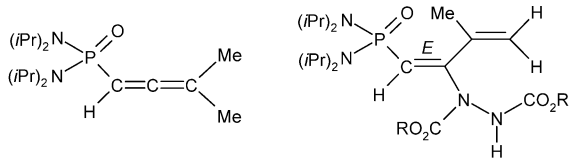


Figure 1. An ORTEP diagram of **22** [P–C(6): 1.748(2), C(6)–C(7): 1.333(3), C(7)–N(1): 1.408(3), N(1)–N(2): 1.397(2) Å].

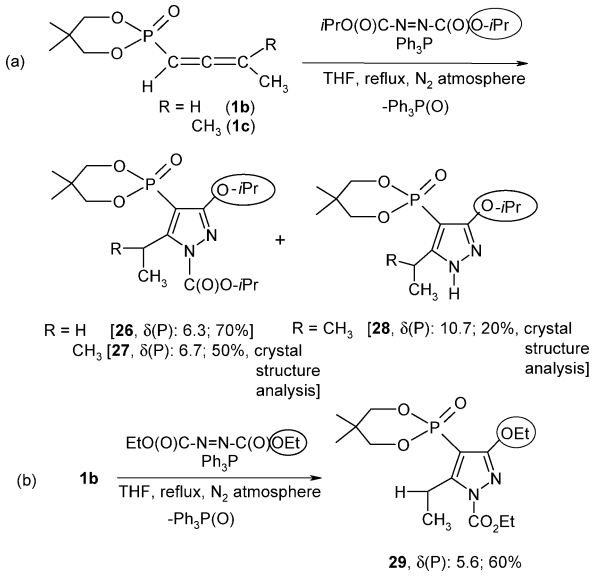
We then performed the above reactions of allenes with DEAD/DIAD in the presence of Ph_3P. Compounds **1b**,**c** readily reacted to afford phosphonopyrazoles **26**–**29** (Scheme 4), whereas the $=CH_2$ terminal allene **1a** re-



23 [δ(P): 19.6]

R = Et [**24**, δ(P): 18.7; 90%]
*i*Pr [**25**, δ(P): 18.9; 90%]

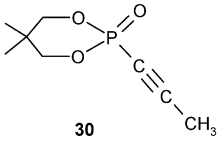
arranged to the acetylene **30**.[6] Of the three solvents (DME, THF and dichloroethane) studied, THF worked best. Although the isolated yields were moderate, the ease of synthesis makes these reactions quite attractive. The major difference between this reaction and the one shown in part (a) of Scheme 1 is the following: for the reaction in Scheme 1 (a), the OEt group on the pyrazole should come from the allenyl esters, whereas the O*i*Pr substituent at the same position in **26**–**28** arises from the DIAD residue. Compound **28** is analogous to **27**, except that the NCO_2–*i*Pr group is hydrolyzed to NH during column chromatography which can be gainfully employed in further synthetic work. This type of product also has not been isolated before.



R = H [**26**, δ(P): 6.3; 70%]
CH_3 [**27**, δ(P): 6.7; 50%, crystal structure analysis]
R = CH_3 [**28**, δ(P): 10.7; 20%, crystal structure analysis]

29, δ(P): 5.6; 60%

Scheme 4.



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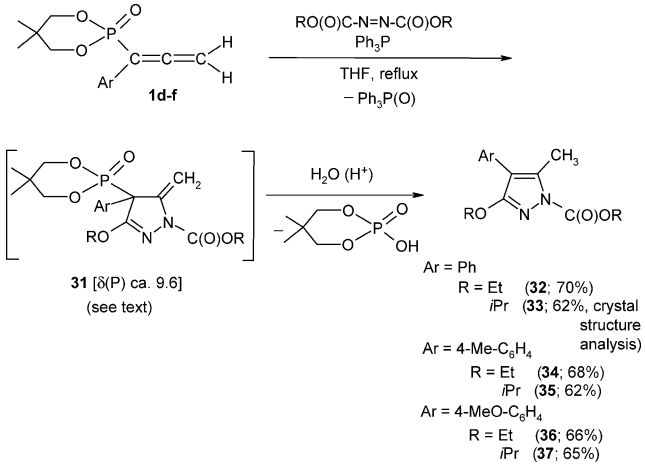
Perhaps more interesting is the reaction shown in Scheme 5 in which tetrasubstituted pyrazoles **32**–**37** were generated by a facile P–C bond-cleavage reaction via the phosphonopyrazole intermediate **31**.[20,21] Species **31** [R = *i*Pr, Ar = Ph] was readily identified by ^1H and ^{31}P NMR spectroscopy. We believe the type of reaction observed here is unprecedented and provides a novel entry into aryl-substituted pyrazoles. This reaction works for α-aryl allenylphosphonates and the separation of pyrazoles **32**–**37** is very easily accomplished.[22] The structure of one of these (**33**) was confirmed by X-ray crystallography (Figure 2). These pyrazole compounds **32**–**37** are fairly stable. Thus, access to different aryl-substituted pyrazoles is possible as a large number of allenes $(RO)_2P(O)C(Ar)CH=C=CH_2$ are accessible via the propargylic alcohols $ArC\equiv CCH_2OH$.



31 [δ(P) ca. 9.6] (see text)

Ar = Ph
R = Et (**32**; 70%)
*i*Pr (**33**; 62%, crystal structure analysis)
Ar = 4-Me-C_6H_4
R = Et (**34**; 68%)
*i*Pr (**35**; 62%)
Ar = 4-MeO-C_6H_4
R = Et (**36**; 66%)
*i*Pr (**37**; 65%)

Scheme 5.

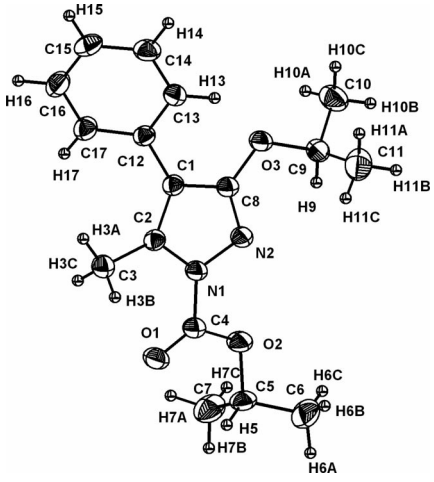
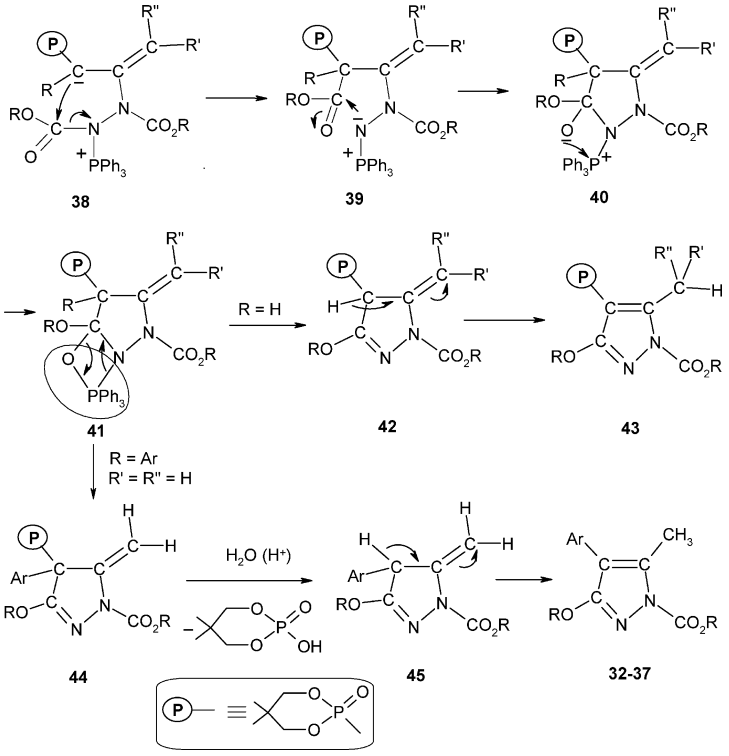


Figure 2. The structure of **33** [N(1)–N(2): 1.381(2) Å].

Based on the available literature, the mechanistic pathway for phosphonopyrazole formation is shown in Scheme 6.[12a,12b] We note the following: (i) the carbanion is formed at the carbon atom α to phosphorus (cf. **38**) thereby leading to substituted pyrazoles; (ii) the OR group on the pyrazole group is derived from the DIAD/DEAD residue and not from the allene; (iii) the cleavage of the P–C bond is very facile and subsequent separation of pyrazoles is very easy. For Ar = Ph and R = *i*Pr, the crystalline compound **33** could be characterized by X-ray crystallography.

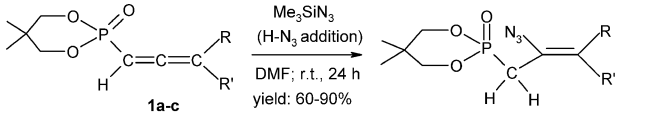
Triazole Formation by Reaction with Trimethysilyl Azide

In the straightforward reaction of allenes **1a**–**c** with trimethylsilyl azide at room temperature, we isolated the hydrolytically unstable non-cyclized azide products **46**–**48** regioselectively and in good yields (Scheme 7). DMF as sol-



Scheme 6.

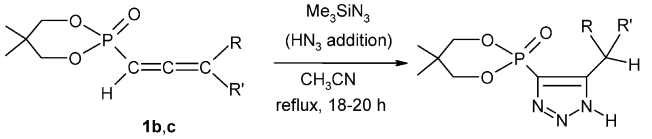
vent was much superior to acetonitrile in this case. Like the reaction with MBH betaine, here also, the nucleophilic part (N_3^-) attaches to the carbon β to the phosphorus. The reaction conducted using the conditions of Huang and coworkers [NaN_3/*t*BuOH/H_2O][23] also gave the azides, but in the case of **1a**, a significant amount of the acetylene **30** was formed.



R, R' = H [**46**; δ(P) 19.4; 80%]
R = H, R' = Me [**47**; δ(P) 19.8, 19.7; 50%]
E/Z ~ 1:2
R, R' = Me [**48**; δ(P): 21.2; 80%]

Scheme 7.

The above reaction when conducted in refluxing CH_3CN gave the triazoles **49** and **50** (50–60% yield based on ^{31}P NMR; 20–40% isolated yield; Scheme 8; Figure 3).[24] Although the isolated yield was not high, it was very easy to separate these compounds.



R = Me; R' = H [**49**, δ(P): 1.5; 40%, X-ray]
R = R' = Me [**50**, δ(P): 2.6; 20%, X-ray]

Scheme 8.

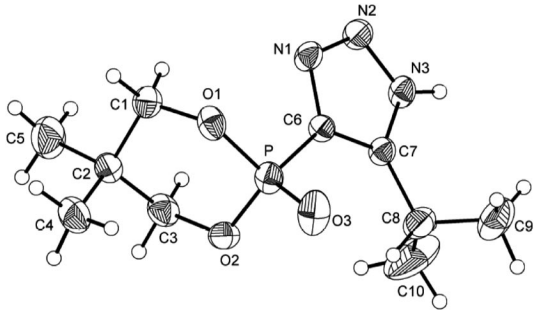
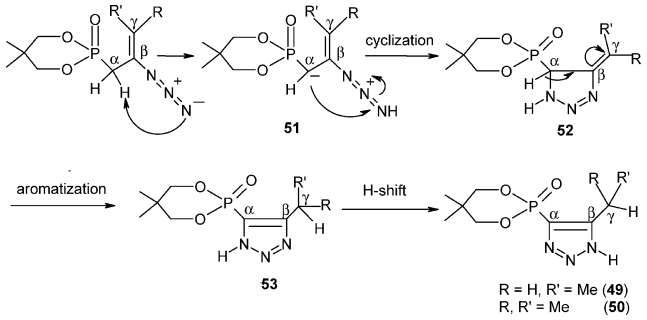


Figure 3. An ORTEP diagram of **50** [P–C(6): 1.768(2) Å; hydrogen-bonding parameters: N(3)–H(3)···O(3′): 0.83(3), 1.93(3), 2.749(3) Å, 167(3)°; symmetry code: 2 – *x*, –0.5 + *y*, 1 – *z*].

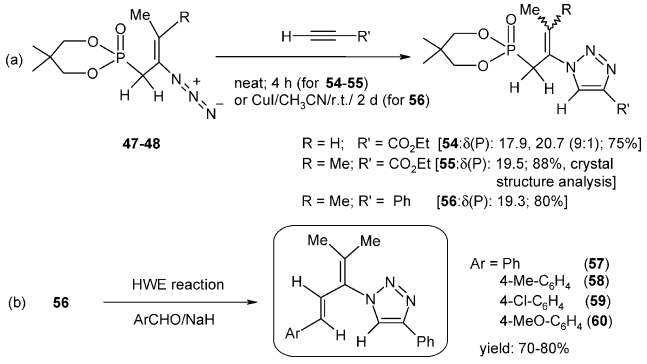
A possible pathway for the formation of triazoles starting from the azide addition products **49** and **50** is shown in Scheme 9. The $–N_3$ group takes a proton from the α carbon to give **51**. Note that the formation of phosphonate carbanions at the α carbon in the presence of a base is well known in Horner–Wadsworth–Emmons (HWE) reactions. Cyclization followed by aromatization and a proton shift leads to triazoles **49** and **50**. Although the precursor triazole **53** should also be fairly stable, we did not observe this form in the X-ray structure of the two compounds isolated in this study. A similar pathway, via the $C–N^-–N^+{\equiv}N$ dipolar form, is also possible, but is not shown in Scheme 9.

Azides undergo 1,3-dipolar cycloaddition reactions with activated acetylenes to give 1,2,3-triazoles[18,25] and hence we treated **48** with ethyl propiolate or phenyl acetylene to obtain the phosphonotriazoles **55** and **56** stereoselectively



Scheme 9.

in high yields. Similarly, **47** and ethyl propiolate led to **54** (Scheme 10, a). In the synthesis of **56**, CuI was needed. The MW-assisted reaction (180 °C, 160 W) in the case of **54** and **55** was also useful and was complete in 10 min. The stereochemistry of **55** was established by X-ray crystallography (Figure 4). Thus, this route offers functionalized phosphonotriazoles with activated acetylenes in a very short time. What is also quite useful is the fact that the phosphonate group can be readily cleaved by means of the HWE reaction.[26] Thus we could obtain phosphorus-free 1,2,3-triazoles **57**–**60** very easily in good yields (Scheme 10, b). This approach opens up a convenient access to diverse phosphorus-free triazoles as three variables − allene, acetylene and the aldehyde − are available.



Scheme 10.

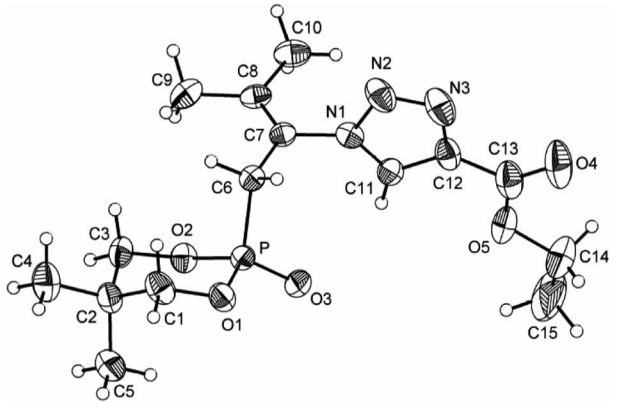


Figure 4. An ORTEP drawing of compound **55** [P–C(6): 1.796(2) Å].

Conclusions

The reaction of allenylphosphonates with the MBH betaine formed from PPh_3/DEAD or DIAD leads directly to phosphonopyrazoles without the prerequisite of an ester group on the allene. In the absence of PPh_3, the $=CMe_2$ terminal allenylphosphonates readily afford substituted phosphono-1,3-butadienes in nearly quantitative yields (^{31}P NMR evidence) under neat (or MW) conditions. A novel phosphate elimination reaction leading to tetrasubstituted pyrazoles has been discovered. The ease of preparation and the low effective cost of our allenylphosphonates are additional assets to this procedure. Stable phosphonotriazoles are obtained readily through a simple Me_3SiN_3-mediated addition of HN_3 to allenylphosphonates at reflux temperature in CH_3CN whereas at room temperature (CH_3CN or DMF), β-azido-allylphosphonates are obtained in high yields. The potential of the β-azido-allylphosphonates is demonstrated by the high-yielding stereoselective synthesis of multisubstituted triazoles by 1,3-dipolar cycloaddition with acetylenes and subsequent HWE reaction, which gives phosphorus-free triazoles. Any of the three ingredients − allene, acetylene or aldehyde − can be varied in the production of this class of triazoles.

Experimental Section

General: Precursors **1a**–**c** were prepared by following literature procedures.[6,8] Acetylene **30** was formed normally under basic conditions, even in the presence of Ph_3P, as mentioned above. Pure **30** [δ(P) = –12.9 ppm] was prepared by treating **1a** with triethylamine.[6,17a]

Allenes ($OCH_2CMe_2CH_2O$)PC(Ar)=C=CH_2 [Ar = Ph (**1d**), 4-Me-C_6H_4 (**1e**), 4-MeO-C_6H_4 (**1f**)] were synthesized by using ($OCH_2CMe_2CH_2O$)PCl and the appropriate propargylic alcohol in 80% yield in a manner similar to that for **1a**–**c**.

Compound 1d: M.p. 110–114 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2976, 2892, 1962, 1933, 1707, 1489, 1271 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 and 1.29 (2s, 6 H), 3.92–3.99 (m, 4 H), 5.35 and 5.38 (2s, 2 H), 7.26–7.60 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.8, 21.9, 32.6 (d, J = 7.0 Hz), 77.3, 78.7, 78.9, 95.2 (d, J = 181.0 Hz), 127.6, 127.7, 128.0, 128.8, 130.5, 130.6, 212.9 (J = 5.0 Hz) ppm. ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.6 ppm. $C_{14}H_{17}O_3P$ (264.3): calcd. C 63.63, H 6.48; found C 63.68, H 6.42.

Compound 1e: M.p. 138–140 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2975, 2886, 1935, 1715, 1481, 1264 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 and 1.30 (2s, 6 H), 2.34 (s, 3 H), 3.92–4.00 (m, 4 H), 5.33 and 5.36 (m, 2 H), 7.15–7.50 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.8, 21.2, 21.9, 32.6 (d, J = 7.0 Hz), 77.3, 77.4, 78.7 (d, J = 14.0 Hz), 95.2 (d, J = 181.0 Hz), 127.4, 127.5, 128.5, 129.5, 137.9, 212.7 (J = 4.0 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.8 ppm. $C_{15}H_{19}O_3P$ (278.3): calcd. C 64.74, H 6.88; found C 64.82, H 6.87.

Compound 1f: M.p. 105–108 °C. IR (KBr): $\tilde{\nu}$ = 3061, 2959, 2895, 1937, 1607, 1512, 1458, 1441, 1258, 1057 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 and 1.30 (2s, 6 H), 3.80 (s, 3 H), 3.92–3.99 (m, 4 H), 5.33–5.36 (m, 2 H), 6.87–7.54 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.6, 21.8,

32.5 (d, J = 7.0 Hz), 55.2, 77.2$_7$, 77.3$_4$, 78.8 (d, J = 14.0 Hz), 94.8 (d, J = 180.0 Hz), 114.2, 122.4, 122.5, 128.8, 128.9, 159.4, 212.3 (J = 4.0 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.5 ppm. $C_{15}H_{19}O_4P$ (294.3): calcd. C 61.22, H 6.51; found C 61.25, H 6.52.

Reaction of Allene 1c with Dialkyl Azodicarboxylates

Synthesis of $(OCH_2CMe_2CH_2O)P(O)CH=C[N(CO_2R)NH-(CO_2R)]C(Me)=CH_2$ [R = Et (21), *i*Pr (22)]: Allene **1c** (0.60 g, 2.77 mmol) was heated with DEAD/DIAD (3.33 mmol) at 150 °C for 30 min. The ^{31}P NMR spectrum showed a single product. Compound **21** or **22** was isolated (≈71%) by using column chromatography (EtOAc/hexane, 1:1, silica gel).

Alternative MW-Assisted Synthesis of 21 and 22: Allene **1c** (0.17 g, 0.77 mmol) and DEAD or DIAD (0.77 mmol) were placed in a 10 mL of conical flask and heated in a microwave reactor for 30 min [180 °C; 160 W]. Compound **21** or **22** was isolated by using column chromatography (EtOAc/hexane, 2:3, silica gel).

Compound 21: Yield quantitative (^{31}P NMR); isolated yield 0.19 g (64%); m.p. 126–128 °C. IR (KBr): $\tilde{\nu}$ = 3196, 2990, 1750, 1593, 1316, 1238, 1057, 1003 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 and 1.18 (2s, 6 H), 1.28 (t, J = 6.4 Hz, 6 H), 1.99 (s, 3 H), 3.85–3.90 (br. m, 4 H), 4.17–4.24 (m, 4 H), 5.26 (s, 1 H), 5.49 (s, 1 H), 5.53 (d, J ≈ 12.0 Hz, 1 H), 8.13 (br., 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.1, 14.4, 20.8, 21.7, 32.3 (d, J = 6.1 Hz), 61.9, 63.2, 76.2 (br.), 98.3 (d, J = 190.4 Hz), 120.7, 139.1, 153.2, 155.4, 159.2, 159.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.4 ppm. $C_{16}H_{27}N_2O_7P$ (390.4): calcd. C 49.22, H 6.97, N 7.17; found C 49.29, H 6.95, N 7.12.

Compound 22: Yield >95% (MW route, ^{31}P NMR); isolated yield 0.23 g (80%); m.p. 138–141 °C. IR (KBr): $\tilde{\nu}$ = 3150, 2976, 1736, 1595, 1541, 1472, 1279, 1107, 1057, 1005 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 and 1.18 (2s, 6 H), 1.28 (d, J = 1.7 Hz, 6 H), 1.29 (d, J = 1.7 Hz, 6 H), 2.00 (s, 3 H), 3.84–3.96 (br. m, 4 H), 4.95–4.99 (br. m, 2 H), 5.28 (s, 1 H), 5.50 (s, 1 H), 5.61 (d, J = 12.4 Hz, 1 H), 7.38 (br., 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.9, 21.0, 21.7, 21.9, 32.3 (d, J = 6.1 Hz), 69.9, 71.7, 76.2 (br.), 98.6 (d, J = 194.1 Hz), 120.7, 139.3, 152.8, 155.1, 159.3, 159.7 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.9 ppm. $C_{18}H_{31}N_2O_7P$ (418.4): calcd. C 51.67, H 7.47, N 6.69; found C 51.66, H 7.44, N 6.64. The X-ray structure of this compound was determined.

Synthesis of the Allene $\{[(CH_3)_2CH]_2N\}_2P(O)CH=C=C(CH_3)_2$ (23): This compound was prepared by a procedure similar to that used for **1a** using $\{[(CH_3)_2CH]_2N\}_2PCl$[27] (3.60 g, 1.35 mmol), $HC{\equiv}CC(CH_3)_2(OH)$ (1.14 g, 1.31 mL, 1.35 mmol) and NEt_3 (1.37 g, 1.88 mL, 1.35 mmol). It was purified by using column chromatography (EtOAc/hexane, 1:1, silica gel). Yield 3.31 g (80%); m.p. 52–54 °C. IR (KBr): $\tilde{\nu}$ = 2971, 2872, 1966, 1647, 1456, 1401, 1366, 1223, 984 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.19–1.31 (2d, 24 H), 1.70 (d, J ≈ 4. 0 Hz, 3 H), 1.71 (d, J ≈ 3. 0 Hz, 3 H), 3.48–3.56 (m, 4 H), 5.22–5.29 (br. m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.7$_0$, 18.7$_2$, 18.9, 21.9, 22.6$_7$, 22.6$_8$, 23.0$_5$, 23.0$_6$, 23.7, 45.4, 45.5, 46.8, 47.3, 86.7 (d, J = 148.8 Hz), 96.0 (d, J = 14.4 Hz), 208.5 ppm. ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.6 ppm. $C_{17}H_{35}N_2OP$ (314.5): calcd. C 64.93, H 11.22, N 8.91; found C 64.80, H 11.21, N 8.98.

Synthesis of $\{[(CH_3)_2CH]_2N\}_2P(O)CH=C[N(CO_2R)NH(CO_2R)]-C(Me)=CH_2$ [R = Et (24), *i*Pr (25)]

Compound 24: Prepared by a procedure similar to that used for **21** using the allene **23** (0.224 g, 0.72 mmol). Yield 0.31 g (90%); m.p. 150–153 °C. IR (KBr): $\tilde{\nu}$ = 3152, 2975, 1748, 1726, 1595, 1541, 1474, 1370, 1304, 1273, 1211, 982 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.22–1.29 (m, 30 H), 2.08 (s, 3 H), 3.52–3.59 (br. m, 4 H), 4.20–4.24 (br. m, 4 H), 5.15 and 5.20 (2s, 2 H), 5.88 (br., 1 H), 6.78 (br., 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.2, 14.3, 22.7, 23.3, 45.4, 45.5, 61.9, 62.7, 115.5 (d, J = 146.8 Hz), 117.8, 140.1, 150.0, 150.3, 154.3, 156.1 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.7 ppm. $C_{23}H_{45}N_4O_5P$ (488.6): calcd. C 56.54, H 9.28, N 11.47; found C 56.50, H 9.18, N 11.70.

Compound 25: Prepared by a procedure similar to that used for **21** using the allene **23** (0.20 g, 0.66 mmol). Yield (isolated): 0.29 g (90%); m.p. 136–138 °C. IR (KBr): $\tilde{\nu}$ = 3158, 2980, 1739, 1591, 1531, 1472, 1373, 1300, 1269, 1107, 984 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.21–1.29 (m, 36 H), 2.10 (s, 3 H), 3.50–3.60 (br. m, 4 H), 4.96–5.02 (br. m, 2 H), 5.18 (s, 2 H), 5.88 (br. d, J = 8.5 Hz, 1 H), 6.74 (br., 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.8$_6$, 21.9$_0$, 22.8, 23.4, 45.4$_9$, 45.5$_4$, 70.0, 71.1, 115.4 (d, J = 146.7 Hz), 117.7, 140.6, 150.3, 150.5, 154.0, 155.8 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.9 ppm. $C_{25}H_{49}N_4O_5P$ (516.7): calcd. C 58.12, H 9.56, N 10.84; found C 58.02, H 9.59, N 10.53.

Preparation of $(OCH_2CMe_2CH_2O)P(O)[C=C(CH_2CH_3)N-(CO_2$*i*$Pr)N=C(O$*i*$Pr)]$ (26): DIAD (1.38 g, 1.35 mL, 6.8 mmol) was added to a stirred solution of allenylphosphonate **1b** (1.15 g, 5.7 mmol) in anhydrous THF (10 mL) under N_2 and the reaction mixture was stirred under reflux. Triphenylphosphane (1.79 g, 6.8 mmol) in THF (10 mL) was added to this mixture through an adding funnel in three portions. The reaction mixture was stirred under reflux for 24 h, cooled, the solvent removed on a rotary evaporator and the residue was purified by column chromatography on silica gel by using ethyl acetate/hexane (1:3) as eluent to afford the product. Yield 1.54 g (70%); m.p. 62–64 °C. IR (KBr): $\tilde{\nu}$ = 2976, 1750, 1561, 1509, 1373, 1306, 1231, 1183, 1107, 1049, 995 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.09 and 1.19 (2s, 6 H), 1.23–1.45 (m, 15 H), 3.29 (br. q, J ≈ 7.0 Hz, 2 H), 4.03–4.16 (m, 4 H), 5.13 and 5.23 (2m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.9, 20.6, 21.5, 21.7, 22.0, 32.5 (d, J = 6.6 Hz), 72.8, 73.0, 75.9, 76.0, 98.2 (d, J = 216.2 Hz), 148.9, 159.2 (d, J = 26.1 Hz), 162.3, 162.4 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.3 ppm. $C_{17}H_{29}N_2O_6P$ (388.4): calcd. C 52.57, H 7.52, N 7.21; found C 52.64, H 7.54, N 7.17.

Preparation of $(OCH_2CMe_2CH_2O)P(O)\{C=C[CH(CH_3)_2]N(CO_2-$*i*$Pr)N=C(O-$*i*$Pr)\}$ (27) and $(OCH_2CMe_2CH_2O)P(O)\{C=C-[CH(CH_3)_2]N(H)N=C(O-$*i*$Pr)\}$ (28): In a procedure similar to that used for **26**, allenylphosphonate **1c** (0.82 g, 3.8 mmol), DIAD (0.92 g, 0.90 mL, 4.5 mmol) and triphenylphosphane (1.20 g, 4.5 mmol) were used. Column chromatography afforded **27** (ethyl acetate/hexane, 1:3) followed by **28** (ethyl acetate/hexane, 1:1). Crystals of **27** and **28** were obtained from dichloromethane/hexane.

Compound 27: Yield 0.76 g (50%); m.p. 72–76 °C. IR (KBr): $\tilde{\nu}$ = 2976, 2880, 1752, 1566, 1472, 1431, 1375, 1316, 1244, 1183, 1105, 1049, 993 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.02 and 1.23 (2s, 6 H), 1.37–1.46 (m, 18 H), 4.00–4.15 (m, 5 H), 5.09–5.12 (m, 1 H), 5.18–5.21 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.5, 21.4, 21.7, 22.0, 22.1, 27.0, 32.5 (d, J ≈ 7.0 Hz), 72.5, 73.1, 76.1, 76.2, 97.0 (d, J ≈ 213.0 Hz), 149.3, 161.9, 162.1, 162.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.7 ppm. $C_{18}H_{31}N_2O_6P$ (402.4): calcd. C 53.72, H 7.76, N 6.96; found C 53.70, H 7.75, N 6.92. The X-ray structure of this compound was determined.

Compound 28: Yield 0.24 g (20%); m.p. 216–218 °C. IR (KBr): $\tilde{\nu}$ = 3181, 3088, 3046, 1557, 1510, 1470, 1327, 1227, 1186, 1129, 1053, 1003 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.10, 1.21 (2s, 6 H), 1.31 (d, J = 7.0 Hz, 6 H), 1.37 (d, J = 6.1 Hz, 6 H), 3.66–3.69 (br. m, 1 H), 4.00 (t, J = 12.6 Hz, 2 H), 4.23 (t, J = 10.5 Hz, 2 H), 4.94–4.98 (br. m, 1 H), 10.18 (br., 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.8, 22.2, 25.6, 32.6, 71.9, 75.3, 75.4, 87.1 (d, J = 226.8 Hz), 158.1 (d, J = 26.7 Hz), 163.6 (d, J = 8.5 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.7 ppm. $C_{14}H_{25}N_2O_4P$ (316.3): calcd. C 53.16, H 7.97, N 8.86; found C 53.26, H 8.09, N 8.88. The X-ray structure of this compound was determined.

Preparation of $(OCH_2CMe_2CH_2O)P(O)[C=C(CH_2CH_3)N(CO_2Et)-N=C(OEt)]$ (29): In a procedure similar to that used for **26**, allenylphosphonate **1b** (0.30 g, 1.5 mmol), DEAD (0.31 g, 0.28 mL, 1.8 mmol) and triphenylphosphane (0.47 g, 1.8 mmol) were used. Column chromatography using 15% ethyl acetate/hexane afforded **29**. Yield 0.32 g (60%); m.p. 100–102 °C. IR (KBr): $\tilde{\nu}$ = 2984, 2936, 1752, 1566, 1509, 1439, 1385, 1314, 1249, 1179, 1053, 995 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.12, 1.15 (2s, 6 H), 1.25 (t, $J \approx$ 7.4 Hz, 3 H), 1.39–1.46 (m, 6 H), 3.31 (q, J = 7.2 Hz, 2 H), 4.01 (t, J = 11.2 Hz, 2 H), 4.17 (t, J = 10.8 Hz, 2 H), 4.38 (q, $J \approx$ 7.2 Hz, 2 H), 4.48 (q, $J \approx$ 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.8, 14.1, 14.5, 20.4, 21.5, 21.9, 32.5 (d, J = 6.5 Hz), 64.1, 65.3, 75.8, 75.9, 96.8 (d, J = 217.2 Hz), 149.4, 160.0 (d, J = 26.0 Hz), 163.1, 163.2 ppm. ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.61 ppm. $C_{15}H_{25}N_2O_6P$ (360.4): calcd. C 50.00, H 6.99, N 7.77; found C 50.11, H 7.03, N 7.81.

Synthesis of the Pyrazole $[C(Ph)=C(CH_3)N(CO_2Et)N=C(OEt)]$ (32): In a procedure similar to that used for **26**, allenylphosphonate **1d** (0.40 g, 1.6 mmol), DEAD (0.33 g, 0.30 mL, 1.9 mmol) and triphenylphosphane (0.50 g, 1.9 mmol) were used. The imine $Ph_3P=NCO_2Et$[22] was separated by column chromatography and the residue was taken up in THF (5 mL) and treated with 6 N HCl (5 mL) for 24 h. Extraction with diethyl ether and purification by column chromatography (ethyl acetate/hexane, 2:98) gave **32**. Yield 0.31 g (70%); m.p. 61–63 °C. IR (KBr): $\tilde{\nu}$ = 2981, 1958, 1898, 1761, 1613, 1593, 1522, 1373, 1325, 1258, 1181, 1063, 1003 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.40, 1.48 (2t, J = 7.1 Hz, 6 H), 2.59 (s, 3 H), 4.42, 4.51 (2q, $J \approx$ 7.1 Hz, 4 H), 7.34–7.46 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.5, 14.4, 14.6, 63.7, 64.8, 112.9, 127.1, 128.4, 129.5, 130.4, 141.9, 150.7, 162.2 ppm. $C_{15}H_{18}N_2O_3$ (274.3): calcd. C 65.68, H 6.61, N 10.21; found C 65.64, H 6.65, N 10.63.

Synthesis of the Pyrazole $[C(Ph)=C(CH_3)N(CO_2iPr)N=C(OiPr)]$ (33): In a procedure similar to that used for **32**, allenylphosphonate **1d** (1.52 g, 6.0 mmol), DIAD (1.46 g, 1.43 mL, 7.2 mmol) and triphenylphosphane (1.90 g, 7.2 mmol) were used. After separating $Ph_3P=NCO_2iPr$,[22] simple crystallization in air afforded **33** after separation of the phosphate $(OCH_2CMe_2CH_2O)P(O)OH$ (less soluble).[19] In a separate experiment, the intermediate phosphonate $(OCH_2CMe_2CH_2O)P(O)CH(Ph)[CN(CO_2iPr)N=C(OiPr)CH=]$ (**31**; >93% purity, the rest was **1d**) was identified [^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.99, 1.17 (2s, 6 H), 1.26–1.42 (m, 12 H), 3.97–4.25 (m, 4 H), 5.02 (d, $J \approx$ 6.0 Hz, 1 H), 5.09–5.19 (m, 2 H), 5.89 (br., 1 H), 7.28–7.69 (m, 5 H) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.5 ppm] prior to hydrolysis, but after separation of $Ph_3P(O)$ and Ph_3P. This compound could also be readily prepared by treating the reaction mixture with 6 N HCl. Yield 1.12 g (62%); m.p. 61–63 °C. IR (KBr): $\tilde{\nu}$ = 2984, 1738, 1611, 1591, 1512, 1375, 1314, 1264, 1181, 1109, 1088, 918 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.38, 1.46 [2d, ^2J(H,H) = 6.0 Hz, 12 H], 2.55 (s, 3 H), 5.16, 5.26 (2m, 2 H), 7.33–7.45 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.7, 21.9, 22.1, 71.8, 71.9, 113.2, 127.0, 128.3, 129.6, 130.7, 141.2, 150.3, 161.4 ppm. $C_{17}H_{22}N_2O_3$ (302.4): calcd. C 67.53, H 7.33, N 9.26; found C 67.51, H 7.30, N 9.20. X-ray structure of this compound was determined.

Synthesis of the Pyrazole $[C(4\text{-}CH_3C_6H_4)=C(CH_3)N(CO_2Et)-N=C(OEt)]$ (34): In a procedure similar to that used for **32**, allenylphosphonate **1e** (0.46 g, 1.7 mmol), DEAD (0.39 g, 0.35 mL, 2.3 mmol) and triphenylphosphane (0.59 g, 2.3 mmol) were used. Extraction with diethyl ether and purification by column chromatography (ethyl acetate/hexane, 2:98) readily gave **34**. Yield 0.34 g (68%); m.p. 67–69 °C. IR (KBr): $\tilde{\nu}$ = 2984, 2919, 1749, 1603, 1526, 1379, 1344, 1265, 1096, 899 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.37, 1.45 (2t, J = 7.2 Hz, 6 H), 2.38 (s, 3 H), 2.55 (s, 3 H), 4.38, 4.47 (2q, $J \approx$ 7.2 Hz, 4 H), 7.21–7.28 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.5, 14.4, 14.6, 21.2, 63.7, 64.7, 112.8, 127.3, 129.1, 129.4, 136.9, 141.6, 150.7, 162.3 ppm. $C_{16}H_{20}N_2O_3$ (288.4): calcd. C 66.65, H 6.99, N 9.72; found C 66.59, H 6.94, N 9.79.

Synthesis of the Pyrazole $[C(4\text{-}CH_3C_6H_4)=C(CH_3)N(CO_2iPr)-N=C(OiPr)]$ (35): In a procedure similar to that for **32**, allenylphosphonate **1e** (0.72 g, 2.6 mmol), DIAD (0.71 g, 0.35 mL, 3.5 mmol) and triphenylphosphane (0.91 g, 3.5 mmol) were used. Yield 0.53 g (62%); m.p. 57–59 °C. IR (KBr): $\tilde{\nu}$ = 2978, 1738, 1607, 1503, 1455, 1379, 1327, 1264, 1200, 1084, 920 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.35, 1.44 [2d, ^2J(H,H) = 6.2 Hz, 12 H], 2.38 (s, 3 H), 2.52 (s, 3 H), 5.15, 5.22 (2m, 2 H), 7.20–7.27 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.7, 21.3, 22.0, 22.1, 71.8, 113.3, 127.7, 129.1, 129.5, 136.8, 141.0, 150.4, 161.5 ppm. $C_{18}H_{24}N_2O_3$ (316.4): calcd. C 68.33, H 7.65, N 8.85; found C 68.22, H 7.62, N 8.82.

Synthesis of the Pyrazole $[C(4\text{-}CH_3OC_6H_4)=C(CH_3)N(CO_2Et)-N=C(OEt)]$ (36): In a procedure similar to that used for **32**, allenylphosphonate **1f** (0.33 g, 1.1 mmol), DEAD (0.25 g, 0.23 mL, 1.4 mmol) and triphenylphosphane (0.38 g, 1.4 mmol) were used. Extraction with diethyl ether and purification by column chromatography (ethyl acetate/hexane) readily gave **36**. Yield 0.22 g (66%); m.p. 58–60 °C. IR (KBr): $\tilde{\nu}$ = 2982, 2935, 1755, 1597, 1528, 1373, 1323, 1258, 1098, 1005 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.38, 1.45 (2t, $J \approx$ 7.0 Hz, 6 H), 3.83 (s, 3 H), 2.55 (s, 3 H), 4.39, 4.47 (2q, $J \approx$ 7.0 Hz, 4 H), 6.94–7.31 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.6, 14.5, 14.7, 55.4, 63.7, 64.8, 112.7, 114.0, 122.7, 130.7, 141.5, 150.8, 158.9, 162.4 ppm. $C_{16}H_{20}N_2O_4$ (304.4): calcd. C 63.14, H 6.62, N 9.20; found C 63.25, H 6.52, N 9.38.

Synthesis of the Pyrazole $[C(4\text{-}CH_3OC_6H_4)=C(CH_3)N(CO_2iPr)-N=C(OiPr)]$ (37): In a procedure similar to that for **32**, allenylphosphonate **1f** (0.32 g, 1.1 mmol), DIAD (0.29 g, 0.28 mL, 1.4 mmol) and triphenylphosphane (0.37 g, 1.4 mmol) was used. Yield 0.24 g (65%); m.p. 59–62 °C. IR (KBr): $\tilde{\nu}$ = 2980, 2936, 1734, 1599, 1503, 1455, 1378, 1321, 1262, 1090, 922 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.35, 1.44 [2d, ^2J(H,H) = 4.0 Hz, 12 H], 2.50 (s, 3 H), 3.84 (s, 3 H), 5.15, 5.20 (2m, 2 H), 6.94–7.30 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.7, 21.9, 22.1, 55.3, 71.7, 71.8, 112.9, 113.8, 123.0, 129.7, 130.7, 140.7, 150.3, 158.6, 161.5 ppm. LC–MS: m/z = 333 $[M + 1]^+$. $C_{18}H_{24}N_2O_4$ (332.4): calcd. C 65.04, H 7.28, N 8.43; found C 65.01, H 7.26, N 8.65.

Preparation of $(OCH_2CMe_2CH_2O)P(O)CH_2C(N_3)=CRR'$ [R = R′ = H (46); R = H, R′ = Me (47); R = R′ = Me (48)]

Compound 46: Me_3SiN_3 (0.132 g, 1.14 mmol) was added to a solution of allene **1a** (0.108 g, 0.57 mmol) in DMF (5 mL) and the mixture was stirred at room temperature for 24 h. Then it was quenched with water and extracted with diethyl ether (3 × 10 mL). The solvent was removed and the product isolated by column chromatography (EtOAc/hexane, 1:1). Yield 0.105 g (80%); m.p. 78–80 °C. IR (KBr): ṽ = 2101, 1630, 1478, 1314, 1263, 1057, 1009 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.01 and 1.10 (2s, 6 H), 2.70 (d, J = 21.5 Hz, 2 H), 3.83–3.89 (m, 2 H), 4.18–4.23 (m, 2 H), 4.87–4.97 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.4, 21.6, 30.6 (d, J = 136.9 Hz), 32.6 (d, J = 6.3 Hz), 75.5 (d, J = 6.5 Hz), 102.7 (d, J = 10.5 Hz), 137.1 (d, J = 11.6 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.4 ppm. $C_8H_{14}N_3O_3P$ (231.2): calcd. C 41.56, H 6.10, N 18.17; found C 41.60, H 6.16, N 18.50.

Compound 47: Prepared by a procedure similar to that used for **46** by using allene **1b** (0.94 g, 4.60 mmol) and Me_3SiN_3 (0.644 g, 5.60 mmol). A mixture of two geometrical isomers ($E/Z \approx 1:2$) was isolated. Yield 0.57 g (50%); m.p. 84–86 °C. IR (KBr): ṽ = 2103, 1655, 1476, 1271, 1057, 1007 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.07 and 1.13 (2s, 6 H), 1.74–1.80 (m, 3 H), 3.03 and 3.10 [2d, J = 20.8 and 21.7 Hz (for the two isomers)], 3.87–4.26 (m, 4 H), 5.84–5.86 and 5.87–5.92 (2m, 1 H, two isomers) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.6, 21.5, 21.6, 32.6, 31.9, 35.9 (2d, J = 137.8 and 138.5 Hz, two isomers), 75.7 (d, J = 6.7 Hz), 126.1 (d, J = 10.8 Hz), 127.5 (d, J = 11.8 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.8, 19.7 ppm (two isomers). LC–MS: m/z = 218 $[(M - N_2) + 1]^+$; the molecular ion was not observed. $C_9H_{16}N_3O_3P$ (245.2): calcd. C 44.08, H 6.58, N 17.13; found C 44.05, H 6.52, N 17.00.

Compound 48: In a procedure similar to that used for **46**, allene **1c** (0.40 g, 1.9 mmol) and Me_3SiN_3 (0.256 g, 2.2 mmol) were used. In this case, column chromatography was not required to purify the compound. Yield 0.38 g (80%; after work up); m.p. 102–104 °C. IR (KBr): ṽ = 2110, 1661, 1476, 1262, 1173, 1065, 922 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.97 and 1.15 (2s, 6 H), 1.73–1.76 (m, 6 H), 3.00 (d, J = 20.8 Hz), 3.79–3.87 (m, 2 H), 4.27–4.31 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.2 and 20.2 (2d, $J \approx$ 3.6 Hz), 21.3, 21.4, 25.9 (d, J = 139.5 Hz), 32.6 (d, J = 6.0 Hz), 75.1 (d, J = 139.5 Hz), 118.7 (d, J =13.6 Hz), 124.1 (d, J = 11.4 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.2 ppm. In the presence of adventitious moisture in $CDCl_3$, the compound is not stable. GC–MS: m/z = 231 $[M - (N_2)]^+$; the molecular ion was not observed. $C_{10}H_{18}N_3O_3P$ (259.2): calcd. C 46.33, H 7.00, N 16.21; found C 46.23, H 7.04, N 15.94.

Preparation of Phosphono-1,2,3-triazole $(OCH_2CMe_2CH_2O)P(O)[CN(H)–N=NC=]CH_2CH_3$ (49): Me_3SiN_3 (0.64 g, 5.60 mmol) was added to a solution of allene **1b** (0.94 g, 4.65 mmol) in acetonitrile (6 mL), and the mixture was heated at reflux for 16 h. At this stage, ^{31}P NMR showed around 60% of **49**. Then it was quenched with water and extracted with diethyl ether (3 × 20 mL). Some insoluble material was observed. This, along with ether solubles, was taken up in diethyl ether and then the solvent was completely removed. The residual solid was washed with dichloromethane and then crystallized from methanol (3–4 mL). Crystals of compound **49** were obtained after 3 d. Yield 0.45 g (40%); m.p. 206–208 °C (decomp.). IR (KBr): ṽ = 3146, 3082, 1562, 1470, 1375, 1269, 1231, 1161, 1059, 1001 cm^{-1}. ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C, TMS): δ = 0.87 (s, 3 H), 1.20 (t, J = 7.6 Hz, 3 H), 1.23 (s, 3 H), 2.83 (q, J = 7.6 Hz, 3 H), 3.99–4.28 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $[D_6]$DMSO, 25 °C, TMS): δ = 13.5, 16.8, 19.7, 21.3 32.0 (d, J = 7.0 Hz), 76.7 (d, J = 6.0 Hz), 138.0 (br.), 152.0 (br.) ppm. ^{31}P NMR (160 MHz, $[D_6]$DMSO, 25 °C, TMS): δ = 1.5 (s) ppm. $C_9H_{16}N_3O_3P$ (245.2): calcd. C 44.08, H 6.58, N 17.13; found C 44.09, H 6.59, N 17.02. The X-ray structure of this sample was determined.

Preparation of Phosphono-1,2,3-triazole $(OCH_2CMe_2CH_2O)P(O)[CN(H)–N=N–C=]CH(CH_3)_2$ (50): Me_3SiN_3 (0.32 g, 2.8 mmol) was added to a solution of allene **1c** (0.50 g, 2.3 mmol) in acetonitrile (6 mL) and the mixture was heated at reflux for 16 h. Then it was quenched with water and extracted with diethyl ether (3 × 20 mL). ^{31}P NMR spectrum at this stage showed that there was around 50% of **50**. The product was isolated as a white solid by column chromatography (EtOAc/hexane, 3:2). Yield (isolated) 0.12 g (20%); m.p. 162–164 °C. IR (KBr): ṽ = 3090, 1562, 1474, 1258, 1175, 1053, 1005 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.96 and 1.30 (2s, 6 H), 1.34 (s, 6 H), 3.65 (septet, $J \approx$ 8.0 Hz, 1 H), 3.95–4.52 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.5, 22.1, 22.2, 24.4, 30.0, 32.7 (d, J = 6.9 Hz), 77.6 (d, J = 6.1 Hz), 131.2 (d, J = 234.2 Hz), 153.2 (d, J = 30.2 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.6 ppm. $C_{10}H_{18}N_3O_3P$ (259.2): calcd. C 46.33, H 7.00, N 16.21; found C 46.32, H 7.10, N 16.47. The X-ray structure of this sample was determined.

Synthesis of $(OCH_2CMe_2CH_2O)P(O)CH_2C[NN=NC(CO_2Et)=CH]=CMeH$ (54): Compound **47** (0.10 g, 0.41 mmol) and $HC{\equiv}CCO_2Et$ (0.048 g, 0.49 mmol) were heated neat at 80 °C (4 h) or by using a microwave oven (10 min). The product was isolated by column chromatography (EtOAc/hexane, 1:1). Compound **54** was isolated as a mixture of two isomers ($E/Z \approx$ 9:1). Yield 0.105 g (75%); m.p. 123–125 °C. IR (KBr): ṽ = 3140, 1705, 1547, 1472, 1271, 1063, 1011 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.96, 1.02 (2s, 6 H), 1.36–1.42 (m, 3 H), 1.93–1.99 (m, 3 H), 3.18, 3.45 [2d, J = 20.5 Hz each, (two isomers), 2 H], 3.75–4.28 (m, 4 H), 4.38–4.45 (m, 2 H), 6.16–6.23 (m, 1 H), 8.32 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.3, 14.3, 21.2, 21.5, 25.8 (d, J = 136.2 Hz), 32.5 (d, J = 6.0 Hz), 59.2 and 61.4 (2s, two isomers), 76.0 (d, J = 6.5 Hz), 124.0 (d, J = 10.9 Hz), 126.4, 127.7 (d, J = 13.5 Hz), 140.0, 160.5 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 17.9 and 20.7 ppm (9:1). LC–MS: m/z = 344 $[M + 1]^+$. $C_{14}H_{22}N_3O_5P$ (343.3): calcd. C 48.97, H 6.46, N 12.23; found C 48.90, H 6.40, N 12.38.

Synthesis of $(OCH_2CMe_2CH_2O)P(O)CH_2C[NN=NC(CO_2Et)=CH]=CMe_2$ (55): Compound **48** (0.10 g, 0.39 mmol) and $HC{\equiv}CCO_2Et$ (0.045 g, 0.46 mmol) were heated neat in a manner similar to that in the preparation of **54**. The product was isolated by column chromatography (EtOAc/hexane, 1:1). Yield 0.12 g (88%); m.p. 120–122 °C. IR (KBr): ṽ = 3160, 1742, 1524, 1451, 1377, 1285, 1215, 1061, 1007 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.98, 1.00 (2s, 6 H), 1.37–1.40 (m, 3 H), 1.57 and 2.00 (2d, $J \approx$ 4 Hz each, 6 H), 3.23 (d, J = 20.0 Hz, 2 H), 3.68 (dd → t, $J \approx$ 11.5 Hz each, 2 H), 4.02 (dd → t, $J \approx$ 10.6 Hz each, 2 H), 4.37–4.28 (m, 2 H), 8.23 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3, 20.3 and 20.6 (2d, J = 3.0 Hz), 21.2, 21.3, 29.0 (d, J = 135.4 Hz), 32.5 (d, J = 6.1 Hz), 61.3, 75.6 (d, J = 6.4 Hz), 120.8 (d, J = 13.1 Hz), 130.0, 138.1 (d, J = 11.2 Hz), 139.3, 160.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.5 ppm. LC–MS: m/z = 358 $[M + 1]^+$. $C_{15}H_{24}N_3O_5P$ (357.3): calcd. C 50.42, H 6.77, N 11.76; found C 50.47, H 6.70, N 12.02. The X-ray structure of this sample was determined. The other isomer in which the positions of the H and R′ groups are reversed was observed only as a minor product (<10%, not isolated).

Preparation of Compound 56: Copper (I) iodide (0.007 g, 0.03 mmol) was added to a 25 mL round-bottomed flask containing a mixture of **48** (0.100 g, 0 40 mmol) and phenyl acetylene (0.040 g, 0.40 mmol) in anhydrous acetonitrile (3 mL). The resulting mixture was stirred for 2 d at room temperature. The solvent was removed under reduced pressure. Compound **56** was purified by column chromatography (silica gel, ethyl acetate/hexane, 1:1). Yield 0.112 g (80%); m.p.125–127 °C. IR (KBr): $\tilde{\nu}$ = 1628, 1480, 1426, 1373, 1281, 1011, 986 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.95, 1.03 (2s, 6 H), 1.64–1.65 (m, 3 H), 2.08–2.09 (m, 3 H), 3.28 (d, J = 20.0 Hz, 2 H), 3.67 (dd → t, $J \approx$ 12.0 Hz each, 2 H), 3.97 (dd → t, $J \approx$ 12.0 Hz each, 2 H), 7.32–7.87 (m, 5 H), 7.98 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.5, 20.7, 21.3, 21.5, 29.1 (d, J = 133.4 Hz), 32.5 (d, J = 6.0 Hz), 75.8 (d, J = 7.3 Hz), 121.2 (d, J = 12.0 Hz), 122.3, 125.8, 125.8, 128.2, 128.9, 130.5, 137.1 (d, J = 10.9 Hz), 146.9 ppm. ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.3 ppm. LC–MS: m/z = 362 $[M + 1]^+$. $C_{18}H_{24}N_3O_3P$ (361.4): calcd. C 59.81, H 6.67, N 11.63; found C 59.88, H 6.69, N 11.73. The X-ray structure of this sample was determined, but we could not model the solvent (water) properly. Details are available with the authors.

Synthesis of 57–60

Typical Procedure for 59: The phosphonate **56** (0.100 g, 0.30 mmol) was dissolved in dry THF (5 mL) and slowly added to a suspension of NaH (0.013 g, 0.60 mmol) in THF (5 mL) at 0 °C and the mixture stirred at this temperature for 0.5 h. Then 4-chlorobenzaldehyde (0.042 g, 0.30 mmol) in THF (2 mL) was added and the mixture was stirred for 2 h. Water (10 mL) was added and the aqueous layer was thoroughly extracted with diethyl ether (3 × 20 mL). The organic layer was collected, dried (Na_2SO_4), filtered and the solvent removed from the filtrate to give a residue that was purified by column chromatography (silica gel, ethyl acetate/hexane, 1:9) to give **59**. Compounds **57**, **58** and **60** were synthesized in a manner similar to compound **59** using same molar quantities.

Compound 57: Yield 0.063 g (75%); m.p. 118 °C. IR (KBr): $\tilde{\nu}$ = 1636, 1483, 1426, 1219, 1019, 949 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.62 (s, 3 H), 2.15 (s, 3 H), 5.80 (d, J = 16.0 Hz, 1 H), 7.20–7.95 (m, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.0, 21.0, 121.7, 122.2, 125.9, 126.8, 128.1, 128.4, 128.8, 129.0, 129.6, 130.7, 131.1, 136.6, 137.1, 147.4 ppm. LC–MS: m/z = 302 $[M + 1]^+$. $C_{20}H_{19}N_3$ (301.4): calcd. C 79.70, H 6.35, N 13.94; found C 79.77, H 6.40, N 14.10.

Compound 58: Yield 0.069 g (78%); m.p. 121–122 °C. IR (KBr): $\tilde{\nu}$ = 1611, 1510, 1424, 1227, 1020 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.62 (s, 3 H), 2.15 (s, 3 H), 2.32 (s, 3 H), 5.77 (d, J = 16.0 Hz, 1 H), 7.11–7.95 (m, 11 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.0, 20.9, 21.3, 121.3, 121.8, 125.9, 126.7, 128.3, 129.0, 129.5, 131.1, 133.8, 136.4, 138.1, 147.4 ppm. LC–MS: m/z = 360 $[M + 1]^+$. $C_{21}H_{21}N_3$ (315.4): calcd. C 79.97, H 6.71, N 13.32; found C 79.90, H 6.51, N 13.48.

Compound 59: Yield 0.070 g (75%); m.p. 60–62 °C. IR (KBr): $\tilde{\nu}$ = 1640, 1489, 1424, 1227, 1090, 1020 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.63 (s, 3 H), 2.16 (s, 3 H), 5.73 (d, J = 16.0 Hz, 1 H), 7.17–7.94 (m, 11 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.0, 21.0, 121.7, 122.7, 125.8, 127.9, 128.2, 128.4, 128.9, 129.0, 130.5, 130.8, 133.7, 135.1, 137.8, 147.5 ppm. $C_{20}H_{18}ClN_3$ (335.8): calcd. C 71.53, H 5.40, N 12.51; found C 71.52, H 5.39, N 12.47.

Compound 60: Yield 0.071 g (76%); m.p. 123–125 °C. IR (KBr): $\tilde{\nu}$ = 1605, 1510, 1424, 1242, 1179, 1032 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.61 (s, 3 H), 2.14 (s, 3 H), 3.79 (s, 3 H), 5.74 (d, J = 15.6 Hz, 1 H), 6.80–7.96 (m, 11 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.0, 21.0, 55.4, 114.2, 120.2, 121.8, 125.8, 128.0, 128.3, 129.0, 129.1, 129.3, 130.7, 131.1, 135.7, 147.3, 159.7 ppm. $C_{21}H_{21}N_3O$ (331.4): calcd. C 76.11, H 6.39, N 12.68; found C 76.08, H 6.41, N 12.78.

X-ray Crystallography: Single-crystal X-ray data were collected with a Bruker AXS-SMART diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by the full-matrix least-squares method using standard procedures.[28] Absorption corrections were carried out by using the SADABS program where applicable. In general all non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a difference Fourier map and refined isotropically.

Crystal Data for 22: $C_{18}H_{31}N_2O_7P$, M = 418.42, orthorhombic, space group $Pca2_1$, a = 17.8584(17), b = 10.7633(10), c = 11.6169(11) Å, V = 2232.9(4) $Å^3$, Z = 4, μ = 0.162 mm^{-1}, data/restraints/parameters: 4720/1/264, R indices $[I > 2\sigma(I)]$: R_1 = 0.0421, wR_2 (all data) = 0.1086.

Crystal Data for 27: $C_{18}H_{31}N_2O_6P$, M = 402.42, monoclinic, space group $P2_1/n$, a = 6.1082(6), b = 18.912(2), c = 19.611(2) Å, β = 92.129(2)°, V = 2263.9(4) $Å^3$, Z = 4, μ = 0.154 mm^{-1}, data/restraints/parameters: 3921/1/272, R indices $[I > 2\sigma(I)]$: R_1 = 0.0809, wR_2 (all data) = 0.2496.

Crystal Data for 28: $C_{14}H_{25}N_2O_4P$, M = 316.33, monoclinic, space group $P2_1/c$, a = 6.9482(6), b = 12.8961(11), c = 19.833(16) Å, β = 99.45(10)°, V = 1753.0(3) $Å^3$, Z = 4, μ = 0.172 mm^{-1}, data/restraints/parameters: 3093/0/200, R indices $[I > 2\sigma(I)]$: R_1 = 0.0426, wR_2 (all data) = 0.1189.

Crystal Data for 33: $C_{17}H_{22}N_2O_3$, M = 302.37, triclinic, space group $P\bar{1}$, a = 10.8487(7), b = 11.0447(7), c = 15.7402(10) Å, α = 95.532(10), β = 105.549(10)°, γ = 106.892(10)°, V = 1707.22(19) $Å^3$, Z = 4, μ = 0.081 mm^{-1}, data/restraints/parameters: 5990/0/407, R indices $[I > 2\sigma(I)]$: R_1 = 0.0484, wR_2 (all data) = 0.1321.

Crystal Data for 49: $C_9H_{16}N_3O_3P$, M = 245.22, monoclinic, space group $P2_1/c$, a = 9.7155(16), b = 10.0431(17), c = 12.475(2) Å, β = 100.510(2)°, V = 1196.8(3) $Å^3$, Z = 4, μ = 0.227 mm^{-1}, data/restraints/parameters: 2359/0/152, R indices $[I > 2\sigma(I)]$: R_1 = 0.0399, wR_2 (all data) = 0.1083.

Crystal Data for 50: $C_{10}H_{18}N_3O_3P$, M = 259.24, monoclinic, space group $P2_1$, a = 6.1317(9), b = 13.7768(19), c = 8.0675(11) Å, β = 102.875(2)°, V = 664.37(16) $Å^3$, Z = 2, μ = 0.208 mm^{-1}, Flack parameter: 0.11(9), data/restraints/parameters: 2607/1/162, R indices $[I > 2\sigma(I)]$: R_1 = 0.0380, wR_2 (all data) = 0.0609.

Crystal Data for 55: $C_{15}H_{24}N_3O_5P$, M = 357.34, triclinic, space group $P\bar{1}$, a = 8.4701(7), b = 9.3757(8), c = 13.0749(11) Å, α = 83.9530(10), β = 89.7080(10), γ = 64.8720(10)°, V = 933.92(14) $Å^3$, Z = 2, μ = 0.175 mm^{-1}, data/restraints/parameters: 3671/0/222, R indices $[I > 2\sigma(I)]$: R_1 = 0.0538, wR_2 (all data) = 0.1368.

CCDC-669797 (for **22**), -669798 (for **27**), -669799 (for **28**), -669800 (for **33**), -669801 (for **49**), -669802 (for **50**), and -669803 (for **55**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Indian Department of Science and Technology (DST), New Delhi for financial support and for the single-crystal

X-ray diffractometer and the University Grants Commission (UGC), New Delhi for equipment [University with Potental for Excellence (UPE) and Centre for Advanced Studies (CAS) programs]. M. C., N. N. B. K. and K. V. S. thank the Council of Scientific & Industrial Research (CSIR) for fellowships.

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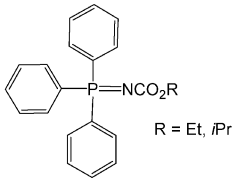
[21] It is important to note that under the conditions employed, we found that phenylallene **2a** did not react (^{1}H NMR evidence).

[22] In addition to these compounds, we also isolated 10–15% of $Ph_3P{=}NCO_2R$ {R = Et [δ = 21.2 ppm] and *i*Pr [δ(P) = 21.2 ppm] from the corresponding reactions with DEAD/DIAD. The compound with R = *i*Pr was isolated and characterized by X-ray crystallography. Details are available with the authors. This compound was obtained previously by a different route, see: S. Bittner, Y. Assaf, P. Krief, M. Pomerantz, B. T. Ziemnicka, C. G. Smith, *J. Org. Chem.* **1985**, *50*, 1712–1718.



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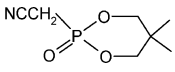

[24] From this reaction we have also isolated ($OCH_2CMe_2CH_2O$)$P(O)CH_2CN$ [δ(P) = 21.2 ppm; X-ray evidence] in ca. 15% yield. As such compounds are known in the literature, we did not proceed further.

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Received: May 20, 2008
Published Online: July 31, 2008

