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Free-radical addition of phosphine sulfides to aryl and hetaryl acetylenes: unprecedented stereoselectivity

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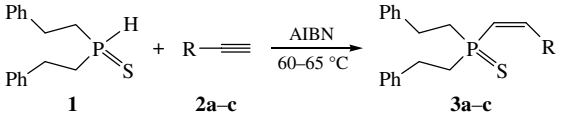
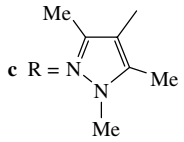
Secondary phosphine sulfides react stereo- and regioselectively with aryl and hetaryl acetylenes in the presence of radical initiators (AIBN, 60–65 °C) in the anti-Markovnikov mode giving *Z*-isomers of the corresponding monoadducts in high yields.

Contrary to nucleophilic addition,[1] free-radical addition to the triple bond is non-stereoselective[2] (with a rare exception[3]). Meanwhile, the stereoselective synthesis of functional alkenes remains a long-standing problem, which is now being mostly solved by using metal complex catalysis.[4]



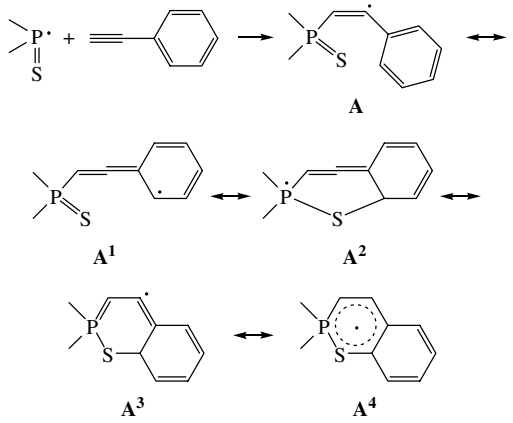
a R = Ph
b R = 4-BrC$_6$H$_4$



Scheme 1

Here, we report on the stereoselective free-radical addition of secondary phosphine sulfide **1** to aryl and hetaryl acetylenes **2a–c**. When initiated by azaisobutyronitrile (AIBN, 60–65 °C), the reaction affords *Z*-isomers of monoadducts **3a–c** in high yields (93–96%) and selectivity (~97%) (Scheme 1).†

Under analogous conditions, oct-1-yne reacts with phosphine sulfide **1** non-selectively to give almost quantitatively *E*- and *Z*-isomers of oct-1-enyl(diphenethyl)phosphine sulfide in a ratio of 1 : 1.



Scheme 2

The stereoselectivity of the addition in the case of aryl acetylenes can be rationalised as follows (Scheme 2): initial radical-adduct **A** is capable of additional stabilising by resonance interaction with adjacent benzene ring (**A^1**) and further through-space spin transfer onto the P=S moiety thus closing the six-membered ring radical species (**A^2**, **A^3**) or **A^4** with the spin distributed over the three multiple bonds and two heteroatoms (P, S).

† *General procedure for the preparation of compounds* **3a–c**.

A mixture of secondary phosphine sulfide **1** (2.0 mmol), organylacetylene **2** (2.0 mmol) and AIBN (5 mg) in 5 ml of dioxane was stirred under an argon atmosphere at 60–65 °C for 5 h (in case of acetylene **2a** and **2c**) and 205 h (when acetylene **2b** was used). Dioxane was then removed under a reduced pressure. The residue was dissolved in diethyl ether, and the solution was passed through a thin layer of Al_2O_3. After solvent evaporation *in vacuo*, *Z*-isomers of tertiary phosphine sulfides **3a–c** of analytical purity grade were obtained.

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX 400 (400.13, 100.69 and 161.98 MHz, respectively) spectrometer. The IR spectra were measured on a Bruker IFS-25 spectrometer in a microlayer in KBr pellets.

Z-(2-Phenethenyl)(diphenethyl)phosphine sulfide **3a**: yellowish oil, yield 93%. ^{1}H NMR ($CDCl_3$) δ: 2.13–2.15 (m, 4H, CH_2P), 2.78–2.80 (m, 4H, CH_2Ph), 5.95 (dd, 1H, =HCP, $^3J_{HH}$ 13.5 Hz, $^2J_{PH}$ 17.5 Hz), 6.94–7.80 (m, 16H, Ph, =*H*CPh). ^{13}C NMR ($CDCl_3$) δ: 28.83 (*C*Ph), 33.94 (d, CP, $^1J_{PC}$ 51.3 Hz), 122.72 (d, =CP, $^1J_{PC}$ 69.4 Hz), 126.45 (C$_p$Ph), 128.18 (C$_o$Ph), 128.31 (C$_p$PhC=), 128.63 (C$_m$Ph), 129.36 (C$_m$PhC=), 129.69 (C$_o$PhC=), 135.87 (d, C$_{ipso}$PhC=, $^3J_{PC}$ 6.3 Hz), 140.58 (d, C$_{ipso}$Ph, $^3J_{PC}$ 15.1 Hz), 145.83 (=*C*Ph). ^{31}P NMR ($CDCl_3$) δ: 36.77. IR (neat, ν/cm^{-1}): 610 (P=S), 640, 690, 750, 770 ($\delta_{CH(Ph)}$), 1450, 1490, 1570, 1590 [C=C(Ph)], 1660 (C=C), 2850, 2920, 2940 (CH), 3010, 3050 [=CH(Ph)], 3080 (=CH). Found (%): C, 76.49; H, 6.52; P, 8.17; S, 8.18. Calc. for $C_{24}H_{25}PS$ (%): C, 76.57; H, 6.69; P 8.23; S 8.52.

Z-2-(4-Bromophenethenyl)(diphenethyl)phosphine sulfide **3b**: white solid, yield 95%, mp 75–76 °C. ^{1}H NMR ($CDCl_3$) δ: 2.11–2.19 (m, 4H, CH_2P), 2.74–2.84 (m, 4H, CH_2Ph), 5.97 (dd, 1H, =HCP, $^3J_{HH}$ 13.3 Hz, $^2J_{PH}$ 17.7 Hz), 6.97 (d, 4H, H$_o$Ph, $^4J_{PH}$ 7.2 Hz), 7.16–7.28 (m, 7H, H$_{p,m}$Ph, =*H*CPhBr), 7.73, 7.54 (d, 4H, H$_{o,p}$PhBr, $^3J_{HH}$ 8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 28.91 (*C*Ph), 33.95 (d, CP, $^1J_{PC}$ 51.1 Hz), 123.34 (d, =CP, $^1J_{PC}$ 72.0 Hz), 124.27 (C$_p$PhBr), 126.69 (C$_p$Ph), 128.29 (C$_o$Ph), 128.85 (C$_m$Ph), 131.62, 131.84 (C$_{o,m}$PhBr), 134.67 (d, C$_{ipso}$PhBr, $^3J_{PC}$ 6.0 Hz), 140.49 (d, C$_{ipso}$Ph, $^3J_{PC}$ 14.1 Hz), 144.80 (=*C*PhBr). ^{31}P NMR ($CDCl_3$) δ: 36.29. IR (KBr, ν/cm^{-1}): 610 (P=S), 640, 690, 750 ($\delta_{CH(Ph)}$), 1455, 1480, 1580 [C=C(Ph)], 1640 (C=C), 2850, 2900 (C–H), 3000, 3050 [=CH(Ph)], 3080 (=CH). Found (%): C, 63.49; H, 5.52; Br, 17.81; P, 7.07; S, 6.88. Calc. for $C_{24}H_{24}BrPS$ (%): C, 63.30; H, 5.31; Br, 17.55; P, 6.80; S, 7.04.

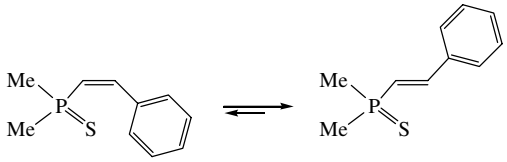
Such an intra-molecular single-electron bonding should secure substituents of the adducts formed in the *cis* (*Z*) disposition.

The lack of the *Z*-stereoselectivity in UV initiation may be explained by the ring-opening of intermediate **A**[4] by the post-isomerization of *Z*-adducts upon applying the extra energy. Indeed, the UV irradiation of *Z*-adduct **3c** results in the formation of the corresponding *E*-isomer.‡

Quantum chemical calculations of the model adduct confirm that, indeed, the *Z*-isomer of (2-phenethenyl)(dimethyl)phosphine sulfide is thermodynamically less preferred than the corresponding *E*-isomer (Scheme 3).

The difference in the MP2/6-311++G**//B3LYP/6-31G* calculated Gibbs free energies is 3.3 kcal mol^{-1}, which corresponds to $Z:E < 0.01$ ratio at equilibrium (350 K).

Thus, the reaction of secondary phosphine sulfides with aryl and hetaryl acetylenes proves to be a general expedient atom-economic stereo- and regioselective synthesis of unsaturated tertiary phosphine suldfides, prospective ligands for the design of metal complex catalysts,[5] intermediates and coordinating solvents for the preparation of conductive nanomaterials[6] and reactive building blocks.[7]



Scheme 3

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*[Z-2-(1,3,5-Trimethyl-1*H*-pyrazol-4-yl)ethenyl](diphenethyl)phosphine sulfide* **3c**: orange oil, yield 95%. ^{1}H NMR ($CDCl_3$) δ: 2.08–2.14 (m, 4H, CH_2P), 2.20, 2.23 (s, 6H, Me-C^{3,5}), 2.81–2.83 (m, 4H, CH_2Ph), 3.67 (s, 3H, MeN), 6.02 (dd, 1H, =HCP, $^3J_{HH}$ 13.4 Hz, $^2J_{PH}$ 18.2 Hz), 6.91–7.25 (m, 11H, Ph, =HCHet). ^{13}C NMR ($CDCl_3$) δ: 11.41 (Me-C^3), 12.78 (Me-C^5), 28.42 (*C*Ph), 33.66 (d, CP, $^1J_{PC}$ 51.1 Hz), 35.84 (MeN), 112.34 (d, =CP, $^1J_{PC}$ 78.5 Hz), 113.81 (d, C^4-Het, $^3J_{PC}$ 6.9 Hz), 126.37 (C$_p$Ph), 127.96 (C$_o$Ph), 128.58 (C$_m$Ph), 136.63 (=*C*Het), 137.24 (C^5-Het), 140.51 (d, C$_{ipso}$Ph, $^3J_{PC}$ 14.9 Hz), 145.02 (C^3-Het). ^{31}P NMR ($CDCl_3$) δ: 38.23. IR (neat, ν/cm^{-1}): 620 (P=S), 640, 690, 750 ($\delta_{CH(Ph)}$), 1420, 1450, 1490, 1600 [C=C(Ph)], 1640 (C=C), 2820, 2950, 2980 (C–H), 3020, 3050 [=CH(Ph)], 3080 (=CH). Found (%): C, 70.49; H, 7.42; N, 6.48; P, 7.17; S, 7.58. Calc. for $C_{24}H_{29}N_2PS$ (%): C, 70.56; H, 7.15; N, 6.86; P, 7.58; S, 7.85.

‡ *Z*-isomer **3c** was UV-irradiated (200 W mercury arc lamp) for 9 h to give quantitatively *E*-isomer.

*[E-2-(1,3.5-Trimethyl-1*H*-pyrazol-4-yl)ethenyl](diphenethyl)phosphine sulfide*: yellowish solid, mp 82–83 °C. ^{1}H NMR ($CDCl_3$) δ: 2.13–2.25 (m, 4H, CH_2P), 2.28, 2.30 (s, 6H, Me-C^{3,5}), 2.84–3.02 (m, 4H, CH_2Ph), 3.70 (s, 3H, MeN), 5.82 (dd, 1H, =HCP, $^3J_{HH}$ 16.7 Hz, $^2J_{PH}$ 25.4 Hz), 7.15–7.26 (m, 10H, Ph), 7.52 (dd, 1H, =*H*CHet, $^3J_{HH}$ 16.7 Hz, $^3J_{PH}$ 24.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 10.01 (Me-C^3), 13.98 (Me-C^5), 27.57 (*C*Ph), 34.65 (d, CP, $^1J_{PC}$ 53.8 Hz), 35.77 (MeN), 111.98 (d, =CP, $^1J_{PC}$ 78.1 Hz), 113.81 (d, C^4-Het, $^3J_{PC}$ 19.8 Hz), 126.03 (C$_p$Ph), 127.88, 128.39 (C$_{o,m}$Ph), 137.74 (=CHet), 139.71 (C^5-Het), 140.77 (d, C$_{ipso}$Ph, $^3J_{PC}$ 14.4 Hz), 146.50 (C^3-Het). ^{31}P NMR ($CDCl_3$) δ: 44.55. IR (KBr, ν/cm^{-1}): 630 (P=S), 690, 750 ($\delta_{CH(Ph)}$), 950 (=CH), 1450, 1490, 1600 [C=C(Ph)], 1620 (C=C), 2850, 2910 (C–H), 3020, 3050 [=CH(Ph)], 3080 (=CH). Elemental analysis data coincide with those for *Z*-isomer.

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