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 monoauctd compounds in high yields.

Contrary to nucleophilic addition,1 free-radical addition to the triple bond is non-stereoselective2 (with a rare exception). Meanwhile, the stereoselective synthesis of functional alkenes remains a long-standing problem, which is now being mostly solved by using metal complex catalysis.3

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 (A1) and further through-space spin transfer onto the P=S moiety thus closing the six-membered ring radical species (A2) or A3 with the spin distributed over the three multiple bonds and two heteroatoms (P, S).

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

A mixture of secondary phosphine sulfide 1 (2.0 mmol), organo-acetylene 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 2e) 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 Al2O3. After solvent evaporation in vacuo, Z-isomers of tertiary phosphine sulfides 3a–c of analytical purity grade were obtained.

The 1H, 13C and 31P NMR spectra were recorded on a Bruker DFX 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-Phenylethenyl)(diphenyl)phosphine sulfide 3a: yellowish oil, yield 93%.1 31P NMR (CDCl3): δ: 2.13–2.15 (m, 4H, CH2P), 2.78–2.80 (m, 4H, CH2Ph), 5.95 (dd, 1H, =HCP, J12,13 13.3 Hz, J1,2 17.7 Hz), 6.94–7.80 (m, 16H, Ph, =HCP). 13C NMR (CDCl3): δ: 28.83 (CPH), 33.94 (d, CP, J1,2 51.3 Hz), 122.72 (d, =CP, J1,2 69.4 Hz), 126.45 (CPh), 128.18 (CPh), 128.31 (CPhC), 128.63 (CPh), 129.36 (CPhC), 129.69 (CPhC), 135.87 (d, CgemPhC, J2,3 6.3 Hz), 140.58 (d, CgemPh, J2,3 15.1 Hz), 145.83 (s=CPH). 31P NMR (CDCl3): δ: 36.77. IR (neat, κ/cm–1): 610 (P=S), 640, 690, 750, 770 (δ(C=PS)), 1450, 1490, 1570, 1590 [C=C(Ph)], 1660 (C=C), 2630, 2629, 3040 (CH), 3100, 3150 (C=CH(Ph)), 3080 (s=CPH). Found (%): C, 76.49; H, 6.52; S, 8.18. Calc. for C40H30PS (%): C, 76.57; H, 6.69; P, 8.23; S, 8.52.

Z-(2-Phenylethenyl)(diphenyl)phosphine sulfide 3b: white solid, yield 95%, mp 75–76 °C.1 31P NMR (CDCl3): δ: 2.11–2.19 (m, 4H, CH2P), 2.74–2.84 (m, 4H, CH2Ph), 5.97 (dd, 1H, =HCP, J1,2 13.3 Hz, J12,13 17.7 Hz), 6.97 (m, 4H, Ph, J12,13 7.2 Hz), 7.16–7.28 (m, 7H, HgemPh, =HFCPhBr), 7.73, 7.54 (d, 4H, HgemPhBr, J5,6 8.3 Hz). 13C NMR (CDCl3): δ: 28.91 (CPH), 33.95 (d, CP, J1,2 51.1 Hz), 123.34 (d, =CP, J1,2 72.0 Hz), 124.27 (CPhBr), 126.69 (CPh), 128.29 (CPh), 128.85 (CPh), 131.62, 131.84 (CgemPhBr), 134.67 (d, CgemPh, J2,3 6.0 Hz), 140.49 (d, CgemPh, J2,3 14.1 Hz), 144.80 (=CPBr). 31P NMR (CDCl3): δ: 36.29. IR (KBr, κ/cm–1): 610 (P=S), 640, 690, 750 (δ(C=PS)), 1455, 1480, 1580 [C=C(Ph)], 1640 (C=C), 2850, 2900 (C=H), 3000, 3050 [s=CPH(Ph)], 3080 (s=CPH). Found (%): C, 63.49; H, 5.52; Br, 17.81; P, 7.07; S, 6.88. Calc. for C40H30Br2PS (%): C, 63.30; H, 5.31; Br, 17.55; P, 6.80; S, 7.04.

- 181 -
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 to 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-phenethylidydimethylphosphine 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 sulfides, prospective ligands for the design of metal complex catalysts, intermediates and coordinating solvents for the preparation of conductive nanomaterials and reactive building blocks.

[Z-2-(1,3,5-Trimethyl-1H-pyrazol-4-yl)ethylidene]diphenylphosphine sulfide 3c: orange oil, yield 95%. ¹H NMR (CDCl₃): δ: 2.08–2.14 (m, 4H, CH₂P), 2.20, 2.23 (s, 6H, Me-C₃), 2.81–2.83 (m, 4H, CH₂Ph), 3.67 (s, 3H, MeN), 6.02 (dd, 1H, =HCP, J_H4 13.4 Hz, J_H3 18.2 Hz), 6.91–7.25 (m, 11H, Ph, =HCPH). ¹⁳C NMR (CDCl₃): δ: 11.41 (Me-C₃), 12.78 (Me-C₃), 28.42 (CPH), 33.66 (d, CP, J_C-P 51.1 Hz), 35.84 (MeN), 71.24 (d, =CP, J_Pc 78.5 Hz), 113.81 (d, C₅H₄N-P, J_Pc 6.9 Hz), 126.37 (C₅Ph), 127.96 (C₅Ph), 136.63 (=CH₃), 137.24 (C₅-Het), 140.51 (d, C₆H₅-P, J_Pc 14.9 Hz), 145.02 (C₅-Het). ³¹P NMR (CDCl₃): δ: 38.23. IR (neat, ν/cm⁻¹): 620 (P=S), 640, 690, 750 (ν₂₂₃Ps), 1420, 1450, 1490, 1600 (C=CPh), 1640 (C=C), 2820, 2950, 2980 (C-H), 3020, 3050 (=CHPh), 3080 (=CH). Found (%): C, 70.49; H, 7.42; N, 6.48; P, 7.17; S, 7.58. Calc. for C₃₂H₂₃N₃P: C, 70.56; H, 7.15; N, 6.86; P, 7.58; S, 7.85.

¹Z-isomer 3c was UV-irradiated (200 W mercury arc lamp) for 9 h to give quantitatively E-isomer.

[E-2-(1,3,5-Trimethyl-1H-pyrazol-4-yl)ethylidene]diphenylphosphine sulfide: yellowish solid, mp 82–83 °C. ¹H NMR (CDCl₃): δ: 2.13–2.25 (m, 4H, CH₂P), 2.28, 2.30 (s, 6H, Me-C₃), 2.84–3.02 (m, 4H, CH₂Ph), 3.70 (s, 3H, MeN), 5.82 (dd, 1H, =HCP, J_H4 16.7 Hz, J_H3 25.4 Hz), 7.15–7.26 (m, 10H, Ph), 7.52 (dd, 1H, =HCPH, J_H3 16.7 Hz, J_H4 24.1 Hz). ¹⁳C NMR (CDCl₃): δ: 10.01 (Me-C₃), 13.98 (Me-C₃), 27.57 (CPH), 34.65 (d, CP, J_Pc 53.8 Hz), 35.77 (MeN), 111.98 (d, =CP, J_Pc 78.1 Hz), 113.81 (d, C₅H₄-N-Het), 117.48 (C₅-Het), 126.03 (C₅Ph), 127.88, 128.39 (C₆H₅-P, J_Pc 19.8 Hz), 137.47 (=CH₂Ph), 139.71 (C₅-Het), 140.77 (d, C₆H₅-P, J_Pc 14.4 Hz), 146.50 (C₅-Het). ³¹P NMR (CDCl₃): δ: 44.55. IR (KBr, ν/cm⁻¹): 630 (P=S), 690, 750 (ν₂₂₃Ps), 950 (=CH), 1450, 1490, 1600 (C=CPH), 1620 (C=C), 2850, 2910 (C-H), 3020, 3050 (=CHPh), 3080 (=CH). Elemental analysis data coincide with those for Z-isomer.

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References

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