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Synthesis of 2-diphenylphosphinoyl-3,5-(diaryl)-3,4-dihydro-2*H*-thiopyrans by the reaction of a bis[(diphenylphosphinoyl)methyl]sulfide with chalcones

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ABSTRACT

The NaH-promoted tandem Michael addition/intramolecular Horner–Wittig reaction of bis(diphenylphosphinoylmethyl)sulfide with chalcones afforded 3,4-dihydro-2*H*-thiopyrans **3a–l** in 78–88% yield.

Organochalcogenium compounds have recently attained a remarkable development as synthetic reagents and intermediates, being the subject of many review articles,[1] and books as well.[2] Among the many classes of organochalcogenium compounds, vinylic chalcogenides have a prominent role.[3] Several methods for the synthesis of vinylic chalcogenides are known, and the Wittig or Horner–Wittig reactions are among the most useful ones. We[4] and others[5] have recently reported a series of convenient methods for the synthesis of vinylic selenides, tellurides, and also sulfides, employing these transformations.

Tandem reaction strategies are among the most powerful methodologies for the conversion of simple substances into structurally more complex organic molecules through a single process. These sequences are usually highly efficient, because formation of new carbon–carbon or carbon–heteroatom bonds is achieved in a successive series of events, without isolating any intermediates. In addition, these reactions often proceed with high regioselectivity.[6] Therefore, tandem reactions have shown to be valuable for the stereoselective synthesis of multifunctionalized cyclic or polycyclic compounds.[7]

It has been reported that the tandem Michael addition-intramolecular Wittig reaction of a five-membered cyclic phosphonium ylide with 8-phenylmenthyl enoates, α,β-unsaturated ketones, esters, and thioesteres afforded multifunctionalized cycloheptene derivatives.[8]

The 3,4-dihydro-2*H*-thiopyrans are a class of cyclic sulfides that have received comparatively little attention, with only a handful of methods available for their preparation.[9] These compounds have been accessed by electroreduction of tetraactivated 4*H*-thiopyrans,[10] double radical cyclization/β-fragmentation of acyclic ω-yne vinyl sulfides,[11] and by reaction of 3-oxo-1-pentene-4-ynes with sodium sulfide.[12]

However, most of the preparations involve the related 3,4-dihydro-2*H*-thiopyran-4-ones, such as the recently reported double C–S bond formation using α,β′-dichloro vinyl ketones and NaSH,[13] and the Pd/Cu-catalyzed cyclization of thioesters with propargyl alcohols.[14] Some other procedures have also been described.[15] In addition, 3,4-dihydro-2*H*-thiopyrans with diverse substitution patterns, including chiral versions, have been obtained by hetero Diels–Alder reactions.[16] The interest in these sulfur-containing six-membered heterocyclic derivatives results from the possibility that they may lead to molecules of pharmacological importance.[17]

Recently, we have described the Wittig–Horner reaction of bis(diphenylphosphinoylmethyl) chalcogenides with carbonyl compounds, such as aldehydes and ketones, to afford symmetrical and unsymmetrical bis-vinylic chalcogenides.[18]

As a continuation of this work, we attempted to perform the reaction of bis(diphenylphosphinoylmethyl) sulfide (**1**) with chalcone in THF; however, an unexpected product was observed, in 79% yield after 6 h at 60 °C, when NaH (2 equiv) was employed as base. This proved to be 2-diphenyl phosphinoyl-3,5-(diphenyl)-3,4-dihydro-2*H*-thiopyran (**3a**).

The transformation demonstrated to be general, and other derivatives were obtained in high yields, as detailed in Table 1.[19] Similar yields were realized when the reaction was carried out during 24 h at room temperature. Shorter reaction times were required when 3 equiv of base was employed; however, employing

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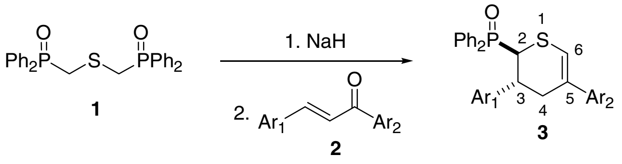
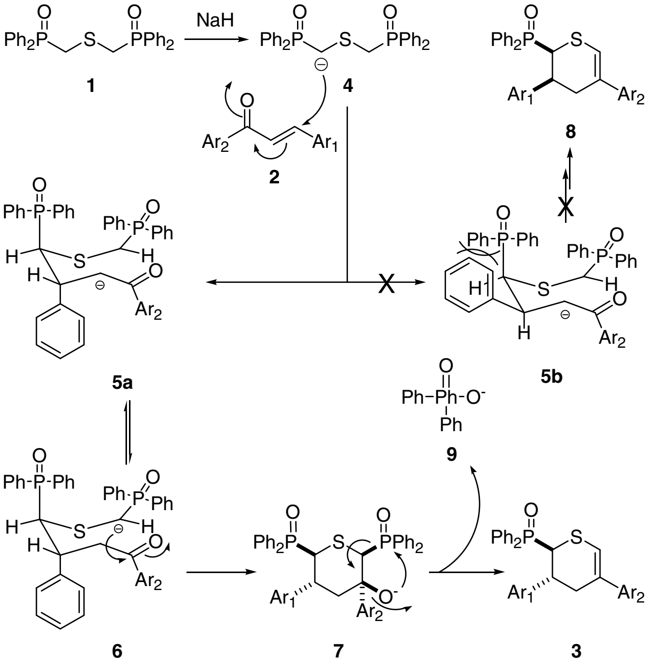
Table 1
Sodium hydride-promoted synthesis of 2-diphenylphosphinoyl-3,5-(diaryl)-3,4-dihydro-2*H*-thiopyrans from bis[(diphenylphosphinoyl) methyl]sulfide and 1,3-diaryl-2-propenones (chalcones)



Entry no.	Product no.	Ar1	Ar2	Yield (%)
1	**3a**	C_6H_5	C_6H_5	79
2	**3b**	C_6H_5	4-Me–C_6H_4	81
3	**3c**	4-Me–C_6H_4	4-Me–C_6H_4	81
4	**3d**	C_6H_5	4-MeO–C_6H_4	78
5	**3e**	4-MeO–C_6H_4	4-MeO–C_6H_4	81
6	**3f**	C_6H_5	4-Cl–C_6H_4	79
7	**3g**	4-Me–C_6H_4	4-MeO–C_6H_4	77
8	**3h**	C_6H_5	4-Br–C_6H_4	88
9	**3i**	4-MeO–C_6H_4	4-Me–C_6H_4	78
10	**3j**	4-Me–C_6H_4	C_6H_5	85
11	**3k**	2-Cl–C_6H_4	4-Cl–C_6H_4	88
12	**3l**	4-Cl–C_6H_4	C_6H_5	86

1.5 equiv NaH gave lower yields either at 60 °C (6 h) or at room temperature (24 h).

The formation of the heterocycles **3a–l** may be rationalized as being the result of the sequence of reactions proposed in Scheme 1. As with most tandem processes including a Wittig olefination, this is the final step. The transformation may be initiated by the Michael addition of anion **4** to the enone **2**, with the Wittig reagent acting as a donor, leading to enolate **5**, which anchors both reactants. This could be followed by proton migration, leading to enolate **6**, in a process favored by the higher acidity of the protons associated to the carbon atom attached to both heteroatoms. In turn, this would set the stage for the intramolecular Horner–Wittig reaction, which would take place through the intermediacy of alkoxide **7** to give **3**, after loss of diphenylphosphinate (**9**).[8a–c]



Scheme 1. Synthesis of 2-diphenylphosphinoyl-3,5-(diaryl)-3,4-dihydro-2*H*-thiopyrans from bis[(diphenyl phosphinoyl) methyl] sulfide and chalcones. Proposed reaction mechanism.

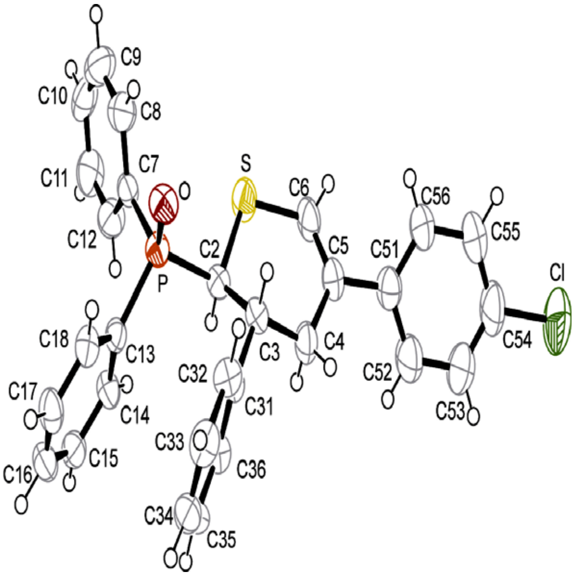


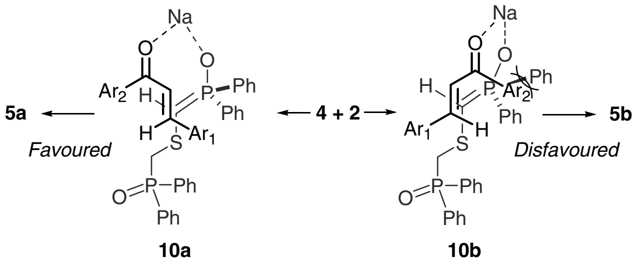
Figure 1. ORTEP view of **3f**, as determined by X-ray crystallography.

Interestingly, the Michael reaction does not involve directly the electronegative atom of the Wittig reagent, which is released after cyclization; therefore, the overall process can be regarded as a [3+3] annulation. The thus synthesized vinyl sulfides **3a–l** were spectroscopically characterized,[20] and their ^1H and ^{13}C NMR spectra indicated that they were formed as a single isomer. However, ^1H NMR signal complexity precluded the determination of the C-2/C-3 substituent relationship.

Therefore, an X-ray measurement of compound **3f** was performed (Fig. 1);[21] as a result, it was confirmed that the 3-aryl group attached to the 3,4-dihydro-2*H*-thiopyran ring was trans to the diphenylphosphinyl group, and that no 2,3-*cis* compounds (**8**), which might have arose from intermediate **5b**, were formed.

This could be a result of a highly diastereoselective Michael addition, proceeding under chelation control through transition state **10a** resulting in Michael adduct **5a** (Scheme 2). The latter would be favored to the alternate transition state **10b**, leading to adduct **5b**, because it avoids unfavorable steric interactions between the aryl moiety attached to the carbonyl and one of the phenyl groups bound to the phosphorous atom.

Analogously, assuming a six-membered chair-like transition state for the Horner–Wittig reaction of the Michael adduct **5** (Scheme 1), transformation of **5a** would be favored over the olefination taking place through the intermediacy of **5b**, also hindering formation of **8**. Alternatively, equilibration between the 2,3-*cis* (**8**) and the 2,3-*trans* forms (**3**) by way of deprotonation–reprotonation of C-1 may lead to the same result; heating a mixture of **3b** with 1 equiv NaH in THF at 60 °C, for 3 h, produced partial deuteration of H-1 after quenching the reaction with D_2O.



Scheme 2. Proposed reaction mechanism of the Michael addition step.

In conclusion, it was demonstrated that the reaction of bis(diphenylphosphinoyl methyl) sulfide with chalcones proceeds with high diastereoselectivity and provides 3,4-dihydro-2*H*-thiopyrans via a tandem Michael addition-intramolecular Horner–Wittig reaction. This represents a novel and stereoselective access to these polysubstituted thiopyran derivatives.

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19. *General procedure*: To a solution of bis[(diphenyl phosphinoyl)methyl] sulfide (1 mmol) in anhydrous THF (10 mL) stirred under an argon atmosphere was added NaH (95%, 51 mg, 2.0 mmol) at room temperature. After 20 min, the appropriate chalcone (1.1 mmol) was added and the reaction mixture was further stirred for 6 h at 60 °C. Then, the reaction was cooled to room temperature, saturated aqueous NH_4Cl (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc–CH_2Cl_2, 5:3:2).
20. *Spectral data of selected compounds*—2-Diphenyl phosphinoyl-3,5-(diphenyl)-3,4-dihydro-2*H*-thiopyran (**3a**): Yield: 79%. Mp 219–221 °C. IR (KBr, cm^{-1}): 695, 747, 1195, 1438. ^1H NMR (400 MHz): δ 2.70 (dd, J = 4.0 and 17.8 Hz, 1H), 3.01 (dd, J = 5.8 and 17.8 Hz, 1H), 3.86–3.89 (m, 1H), 3.95–4.00 (m, 1H), 6.23 (s, 1H), 7.12–7.27 (m, 10H), 7.40–7.52 (m, 6H), 7.79–7.84 (m, 2H), 7.93–7.97 (m, 2H). ^{13}C NMR (50 MHz): δ 30.5 (d, $J_{P–C}$ = 2.4 Hz), 36.6, 42.1 (d, $J_{P–C}$ = 68.0 Hz), 115.1, 124.8, 126.8, 126.9, 127.4, 128.1 (d, $J_{P–C}$ = 11.8 Hz), 128.2, 128.4, 128.6 (d, $J_{P–C}$ = 11.5 Hz), 130.9 (d, $J_{P–C}$ = 8.8 Hz), 131.0 (d, $J_{P–C}$ = 101.1 Hz), 131.7 (d, $J_{P–C}$ = 2.7 Hz), 131.9 (d, $J_{P–C}$ = 2.0 Hz), 132.0 (d, $J_{P–C}$ = 8.8 Hz), 132.2 (d, $J_{P–C}$ = 97.4 Hz), 132.4, 141.4, 143.5 (d, $J_{P–C}$ = 10.1 Hz). MS (*m*/*z*): 452 (M^+, 8), 250 (100), 218 (12), 217 (12), 215 (14), 203 (38), 202 (20), 201 (24), 173 (19), 115 (12), 91 (46), 77 (21), 47 (13). Anal. Calcd for $C_{29}H_{25}OPS$: C, 76.97; H, 5.57. Found: C, 77.31; H, 5.51. 2-Diphenylphosphinoyl-3,5-ditolyl-3,4-dihydro-2*H*-thiopyran (**3c**): Yield: 81%. Mp 232–234 °C. IR (KBr, cm^{-1}): 700, 801, 1185, 1436. ^1H NMR (400 MHz): δ 2.26 (s, 3H), 2.29 (s, 3H), 2.67 (dd, J = 4.2 and 17.7 Hz, 1H), 2.96 (dd, J = 5.7 and 17.7 Hz, 1H), 3.86–3.88 (m, 1H), 3.91–3.97 (m, 1H), 6.16 (s, 1H), 6.99–7.06 (m, 6H), 7.13 (d, J = 8.2, 2H), 7.38–7.42 (m, 4H), 7.45–7.49 (m, 2H), 7.77–7.81 (m, 2H), 7.92–7.97 (m, 2H). ^{13}C NMR (100 MHz): δ 20.9 (2C), 30.5 (d, $J_{P–C}$ = 2.9 Hz), 36.2, 42.2 (d, $J_{P–C}$ = 67.3 Hz), 114.1, 124.6, 127.3, 128.1 (d, $J_{P–C}$ = 11.7 Hz), 128.5 (d, $J_{P–C}$ = 11.7 Hz), 128.9, 129.0, 130.8 (d, $J_{P–C}$ = 8.8 Hz), 131.0 (d, $J_{P–C}$ = 101.0 Hz), 131.5 (d, $J_{P–C}$ = 2.9 Hz), 131.8 (d, $J_{P–C}$ = 2.9 Hz), 132.0 (d, $J_{P–C}$ = 8.8 Hz), 132.3 (d, $J_{P–C}$ = 97.3 Hz), 132.3, 136.4, 136.5, 138.6, 140.5 (d, $J_{P–C}$ = 10.2 Hz). MS (*m*/*z*): 480 (M^+, 9), 280 (7), 279 (25), 278 (100), 277 (12), 246 (10), 201 (11), 105 (22). Anal. Calcd for $C_{31}H_{29}OPS$: C, 77.47; H, 6.08. Found: C, 77.33; H, 6.04.2-Diphenylphosphinoyl-3,5-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-thiopyran (**3e**): Yield: 81%. Mp 120–124 °C. IR (KBr, cm^{-1}): 1181, 1252, 1512, 1609. ^1H NMR (400 MHz): 2.64 (dd, J = 4.1 and 17.5 Hz, 1H), 2.95 (dd, J = 5.4 and 17.5 Hz, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 3.84–3.87 (m, 1H), 3.88–3.92 (m, 1H), 6.11 (s, 1H), 6.72 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 7.39–7.48 (m, 6H), 7.76–7.81 (m, 2H), 7.92–7.96 (m, 2H). ^{13}C NMR (100 MHz): δ 31.1 (d, $J_{P–C}$ = 2.9 Hz), 36.1, 42.3 (d, $J_{P–C}$ = 68.1 Hz), 55.0, 55.1, 113.2, 113.5, 113.6, 125.9, 128.1 (d, $J_{P–C}$ = 11.7 Hz), 128.4 (d, $J_{P–C}$ = 11.0 Hz), 128.5, 130.8 (d, $J_{P–C}$ = 8.8 Hz), 131.1 (d, $J_{P–C}$ = 101.0 Hz), 131.5 (d, $J_{P–C}$ = 2.9 Hz), 131.8 (d, $J_{P–C}$ = 2.9 Hz), 131.9 (d, $J_{P–C}$ = 8.8 Hz), 132.1, 132.4 (d, $J_{P–C}$ = 97.3 Hz), 134.2, 135.6 (d, $J_{P–C}$ = 10.2 Hz), 158.3, 158.5. MS (*m*/*z*): 512 (M^+, 6), 311 (24), 310 (100), 309 (11), 121 (19), 77 (10). Anal. Calcd for $C_{31}H_{29}O_3PS$: C, 72.64; H, 5.70. Found: C, 72.20; H, 5.69. 2-Diphenylphosphinoyl-5-(4-chlorophenyl)-3-phenyl-3,4-dihydro-2*H*-thiopyran (**3f**): Yield: 79%. Mp 205–207 °C. IR (KBr, cm^{-1}): 697, 748, 1193, 1438. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.64 (dd, J = 3.9 and 17.9 Hz, 1H), 3.00 (dd, J = 5.7 and 17.9 Hz, 1H), 3.86–3.88 (m, 1H), 3.92–3.98 (m, 1H), 6.24 (s, 1H), 7.04–7.07 (m, 2H), 7.15–7.23 (m, 7H), 7.38–7.50 (m, 6H), 7.79–7.84 (m, 2H), 7.91–7.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 30.2 (d, $J_{P–C}$ = 2.2 Hz), 36.4, 42.5 (d, $J_{P–C}$ = 68.1), 115.8, 126.0, 127.0, 127.3, 128.2 (d, $J_{P–C}$ = 11.7 Hz), 128.3, 128.4, 128.6 (d, $J_{P–C}$ = 11.0 Hz), 130.8 (d, $J_{P–C}$ = 8.8 Hz), 130.9 (d, $J_{P–C}$ = 101.0 Hz), 131.1, 131.8 (d, $J_{P–C}$ = 2.9 Hz), 131.9 (d, $J_{P–C}$ = 8.8 Hz), 131.9 (d, $J_{P–}$ = 2.2 Hz), 132.0 (d, $J_{P–C}$ = 97.3), 132.5, 139.7, 143.3 (d, $J_{P–C}$ = 10.2 Hz). MS (*m*/*z*): 486 (M^+, 5), 286 (32), 285 (26), 284 (100), 215 (33), 203 (82), 202 (49), 201 (55), 125 (27), 115 (22), 91 (75),77 (48), 51 (23). Anal. Calcd for $C_{29}H_{24}ClOPS$: C, 71.52; H, 4.97. Found: C, 70.93; H, 5.02.
21. A colorless crystal of 0.37 × 0.09 × 0.06 mm was used for X-ray diffraction on a Bruker diffractometer. Mo Kα radiation (λ = 0.71075 Å), graphite monochromator. Reflections collected = 20,571, unique reflections = 4186, R_{int} = 0.1129. Crystallographic data: Molecular formula = $C_{29}H_{24}ClOPS$; M = 486.96; monoclynic system, space group $P2_1/c$, a = 20.4595(12) Å, α = 90°, b = 5.8525(4) Å, β = 111.220(4)°, c = 22.0080(13) Å, γ = 90°, V = 2456.5(3) A^3, Z = 4, d = 1.317 g/cm^3. The structure was solved by the direct method and expanded using difference Fourier techniques, refined by the program and method (SHELXS-97). Hydrogen atoms were fixed at calculated positions. Final R indices [$I > 2.0\sigma I$] R_1 = 0.0576, wR_2 = 0.1380, S = 1.043. Crystallographic data (excluding structure factors) for the structure **3f** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 695347. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).