^{1}H NMR δ 1.05 (t, 3 H, J = 7 Hz), 2.26 (s, 3 H), 2.41 (q, 2 H, J = 7 Hz), 2.70 (m, 2 H), 3.05 (m, 2 H)], **1-(acetylthio)-4-methyl-3-pentanone (6c)** [^{1}H NMR δ 1.11 (d, 6 H, J = 7 Hz), 2.26 (s, 3 H), 2.40 (q, 1 H, J = 7 Hz), 2.73 (m, 2 H), 2.98 (m, 2 H)], and **5-(acetylthio)-2-pentanone (15)**[19] [bp 120–122 °C at 12 Torr; ^{1}H NMR δ 1.83 (t, 2 H, J = 7 Hz), 2.20 (s, 3 H), 2.38 (s, 3 H), 2.56 (t, 2 H, J = 7 Hz), 2.86 (t, 2 H, J = 7 Hz)] were synthesized independently, following literature procedures. Comparison of these authentic materials with the cleavage products of the dioxetane decomposition reaction showed identical spectral and physical data.

H_2O_2 Elimination Products from Allylic Hydroperoxides. 2,3-Dimethylthiophene (7a)[22] [^{1}H NMR δ 2.08 (s, 3 H), 2.26 (s, 3 H), 6.70 (d, 1 H, J = 5 Hz), 6.90 (d, 1 H, J = 5 Hz)] and **3-ethyl-3-methylthiophene (7b)**[23] [^{1}H NMR δ 1.08 (t, 3 H, J = 6 Hz), 2.25 (s, 3 H), 2.36 (q, 2 H, J = 6 Hz), 6.65 (d, 1 H, J = 5 Hz), 6.82 (d, 1 H, J = 5 Hz)] were identified by their literature ^{1}H NMR spectra.

Sulfoxides. The sulfoxides were prepared in analogy to a procedure described by Krug and Boswell.[24] Samples of 100 mmol of the thioenol ethers were dissolved in 40 to 50 mL of acetone and cooled to 0 °C. An equimolar amount of H_2O_2 (30%) was slowly added to the solution so that the temperature never exceeded 8 °C. After 50 h at 0 °C, the solvent was removed on a rotor-evaporator. The residue was extracted with chloroform and the organic layer was dried over $MgSO_4$. Chloroform was removed on a rotor-evaporator and subsequently in vacuo at room temperature. Distillation of the sulfoxides at low pressure (10^{-4} Torr) yielded decomposition products only.

4,5-Dimethyl-2,3-dihydrothiophene 1-oxide (5a): ^{1}H NMR δ 1.86 (s, br, 3 H), 2.03 (s, br, 3 H), 2.73 (m, 2 H), 3.36 (m, 2 H); IR 1650 (C=C), 1030 cm^{-1} (S=O); UV (MeCN) λ_{max} = 260 nm.

4-Ethyl-5-methyl-2,3-dihydrothiophene 1-oxide (5b): ^{1}H NMR δ 1.08 (t, 3 H, J = 8 Hz), 2.01 (m, 3 H), 2.27 (q, 2 H, J = 8 Hz), 2.70 (m, 2 H), 3.34 (m, 2 H); IR 1645 (C=C), 1020 cm^{-1} (S=O); UV (MeCN) λ_{max} = 262 nm.

4-Isopropyl-5-methyl-2,3-dihydrothiophene 1-oxide (5c): ^{1}H NMR δ 1.06 (d, 6 H, J = 7 Hz), 1.84 (m, 3 H), 2.79 (m, 2 H + C*H*(CH$_3$)$_2$), 3.10 (m, 2 H); IR 1640 (C=C), 1025 cm^{-1} (S=O); UV (MeCN) λ_{max} = 265 nm.

5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran 1-oxide (20): ^{1}H NMR δ 1.68 (s, br, 3 H), 1.81 (s, br, 3 H), 2.11 (m, 4 H), 2.84 (m, 2 H); IR 1640 (C=C), 1020 cm^{-1} (S=O); UV (MeCN) λ_{max} = 263 nm.

Supplementary Material Available: ^{1}H NMR spectra of **2a–c**, **3a**, **4a**, **9**, and **15** and ^{13}C NMR spectra of **2a–c** (9 pages). Ordering information is given on any current masthead page.

(22) Janda, M.; Srogl, J.; Nemec, M.; Vopatrna, P. *Synthesis* **1972**, 545.
(23) Gronowitz, S.; Cederlund, B.; Hornfeld, A. B. *Chem. Scr.* **1974**, *5*, 217.
(24) Krug, R. C.; Boswell, D. E. *J. Heterocycl. Chem.* **1967**, *4*, 309.

Reaction of Phosphole Sulfides with Diazoalkanes as a New Route to Phosphinines

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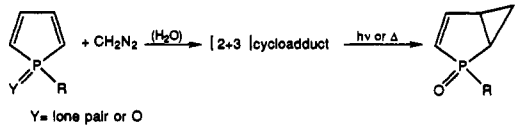
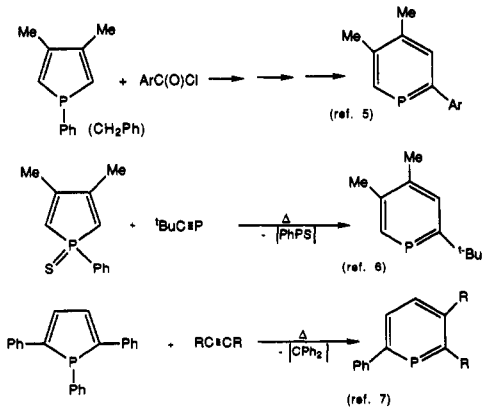
The reaction of ethyl diazoacetate with 1-(methylthio)-3,4-dimethylphosphole 1-sulfide (**6**) in refluxing xylene leads to the corresponding diene–carbene [2 + 1] cycloadduct **7**. The stereochemistry of **7** was established by X-ray crystal structure analysis. Compound **7** is converted into 2-(ethoxycarbonyl)-4,5-dimethylphosphinine (**4**) upon reaction with triphenyl phosphite at 160 °C. On the basis of the X-ray data, the proposed mechanism includes the opening of the cyclopropane ring of **7** with selective phosphorus-assisted migration of the ethoxycarbonyl group. This kind of chemistry can be transposed to a 2,2′-biphosphole to prepare a 2,2′-biphosphinine.

Surprisingly, the reaction of phospholes with diazoalkanes has been the subject of only a few studies.[1-3] In all cases, the reaction led to the corresponding homophospholes. In one instance, the thermal or photochemical



cleavage of the bicyclic system gave para-bridged six-membered ring dimers.[4] On the other hand, three methods for the conversion of phospholes into phosphinines have been described in the literature. When applied



to reasonably accessible 2,2′-biphospholes,[8,9] none of these

(1) Campbell, I. G. M.; Cookson, R. C.; Hocking, M. B.; Hughes, A. N. *J. Chem. Soc.* **1965**, 2184.
(2) Oebels, D.; Klämer, F.-G. *Tetrahedron Lett.* **1989**, *30*, 3525.
(3) Isaacs, N. S.; El-Din, G. N. *Tetrahedron* **1989**, *45*, 7083.
(4) Hughes, A. N.; Srivanavit, C. *Can. J. Chem.* **1971**, *49*, 874.
(5) Mathey, F. *Tetrahedron Lett.* **1979**, 1753. Alcaraz, J.-M.; Brèque, A.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 1565. Alcaraz, J.-M.; Deschamps, E.; Mathey, F. *Phosphorus Sulfur* **1984**, *19*, 45.
(6) Rösch, W.; Regitz, M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 931.
(7) Charrier, C.; Bonnard, H.; Mathey, F. *J. Org. Chem.* **1982**, *47*, 2376.

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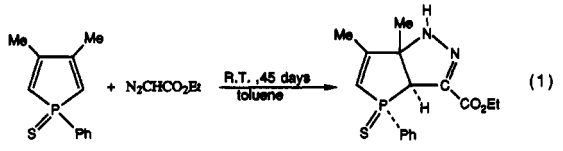
methods provided the expected 2,2′-biphosphinines.[10] The reactions were probably blocked by steric hindrance of the bicyclic system. We were thus interested in an alternative conversion technique, which would circumvent this limitation. We chose to reinvestigate the reaction of phospholes with diazoalkanes as a potential route to phosphinines because we felt that this technique would be less sensitive to steric hindrance than those previously described.

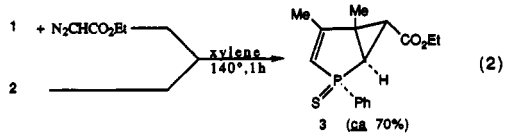
Results and Discussion

In order to prevent a side reaction of the diazoalkane at the phosphorus lone pair, we selected 1-phenyl-3,4-dimethylphosphole 1-sulfide (1)[11] as our substrate. The choice of a *P*-sulfide enabled easy reduction to the corresponding phosphine in a subsequent step of the conversion scheme. Besides, the corresponding oxide is not stable as a monomer.[12] The reaction of 1 with ethyl diazoacetate at room temperature afforded the expected [2 + 3] cycloadduct 2 (eq 1). The regioselectivity of the cyclo-



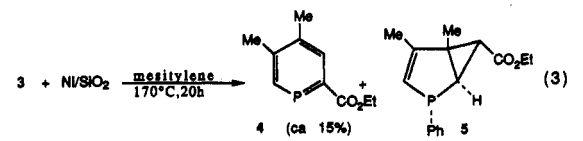
1 2 (53%) (1)

addition was established on the basis of the ^{13}C NMR spectrum. The ethoxycarbonyl-substituted carbon appears at 161.58 ppm with a strong ^2J(C–P) coupling of 22.9 Hz (DMSO-d_6). The β-carbon at the junction resonates at low field [δ 86.0, ^2J(C–P) = 13.4 Hz], confirming the presence of a Cβ–N bond. The ^1H NMR spectrum shows a characteristic broad NH resonance at 6.65 ppm ($CDCl_3$). The α-CH proton [δ 3.80, ^2J(H–P) = 5.5 Hz ($CDCl_3$)] is only weakly coupled with phosphorus and, thus, is trans to the P=S bond.[13] As expected, the regiochemistry is similar to that observed in the reaction of CH_2N_2 with 1-phenyl-3,4-dimethylphosphole[2] and the cycloaddition takes place at the less hindered side of the phosphole sulfide. When carrying out the reaction of 1 with ethyl diazoacetate at high temperature or when heating 2, elimination of nitrogen takes place and the new bicycle 3 is obtained (eq 2). We assume that 3 has the same stereochemistry as



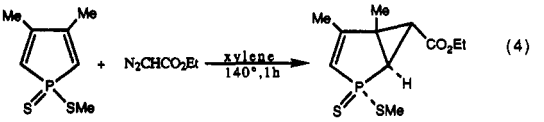
3 (ca 70%) (2)

7. This assumption is based upon the fact that the couplings within the P–CH–CH–CO_2Et unit are similar in both compounds. As expected, the elimination of N_2 takes place with retention of stereochemistry at the junction. We, then, investigated in some depth the conversion of 3 into phosphinine. Our assumption was that, since 3 is isomeric with a dihydrophosphinine sulfide, it could be converted into the corresponding phosphinine via reduction and cleavage of the P–Ph bond with nickel.[5] The reaction of 3 with nickel supported over silica indeed afforded the 2-(ethoxycarbonyl)-4,5-dimethylphosphinine (4) together with the tervalent homophosphole 5 (eq 3).



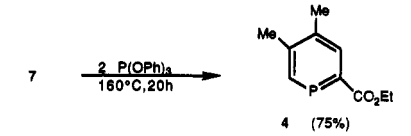
4 (ca 15%) 5 (3)

The phosphinine 4 was characterized by a ^{31}P NMR resonance at +202.5 ppm and the homophosphole 5 by a resonance at −5.2 ppm (toluene). The homophosphole was retransformed into its *P*-sulfide 3 by reaction with sulfur at room temperature, whereas the phosphinine 4 remained unaltered. Then, 4 was purified by chromatography. Alternatively, 3 was first reduced either by Bu_3P or Zn/Hg, or alkylated at sulfur by methyl triflate and, then, reduced by NaH[14] to give 5, which was subsequently treated by nickel over silica. In both routes, the yield of 4 remained low however. Obviously, the weak point of this scheme was the cleavage of the P–Ph bond by nickel. We thus decided to investigate a similar route starting from the easily made 1-(methylthio)-3,4-dimethylphosphole 1-sulfide (6).[15] Upon heating, the reaction of 6 with ethyl diazoacetate directly led to the homophosphole 7 (eq 4).



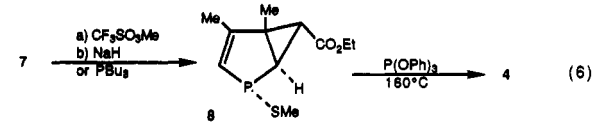
6 7 (75%) (4)

The precise stereochemistry of 7 was established by X-ray crystal structure analysis. The two most important points are that S_1 and C_5 (P=S and CCO_2Et) are on the same side of the former phosphole ring and that CO_2Et and P are on the opposite sides of the cyclopropane plane. The reaction of 7 with triphenyl phosphite (Zn/Hg or Ni/SiO_2 are less efficient) directly gave the phosphinine 4 in good yield (eq 5). Alternatively, 7 was first reduced into the



4 (75%) (5)

tervalent homophosphole 8, which was converted to 4 by reaction with 1 equiv of triphenyl phosphite (eq 6). Since

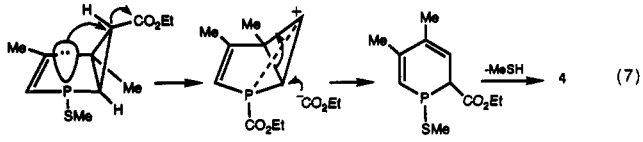


8 (6)

reaction of sulfur with 8 leads to pure 7, 8 and 7 must have the same stereochemistry. The structure of the phosphinine 4 was rather puzzling at first sight. Indeed, the ethoxycarbonyl substituent is now on the α carbon. This fact is unambiguously established by the strong ^2J($PCCO_2$Et) coupling of 24.6 Hz. Besides, the ^1H NMR spectrum of 4 displays one α proton at 8.50 ppm [^2J(H–P) = 39.7 Hz] and one β proton at 8.4 ppm [^3J(H-P) = 3.5 Hz]. All these data are compatible with those recorded

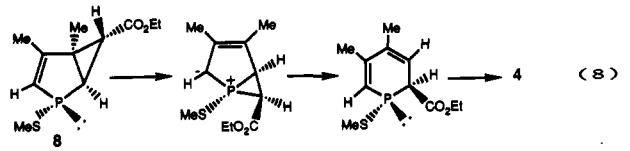
(8) Mathey, F.; Mercier, F.; Nief. F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 2077.
(9) Mercier, F.; Holand, S.; Mathey, F. *J. Organomet. Chem.* **1986**, *316*, 271.
(10) 2,2′-Biphosphinines are the phosphorus analogues of 2,2′-bipyridines and might have impact in coordination chemistry. Only one other route to these ligands has been reported by our laboratory starting from 2-bromophosphinines, see: Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667.
(11) The corresponding phosphole is easily prepared in high yield: Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.
(12) The stability of monomeric 1-phenyl-3,4-dimethylphosphole oxide is discussed in Quin, L. D.; Xia-Ping Wu. *Heteroatom. Chem.* In press.
(13) Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds; VCH Publishers: Deerfield Beach, 1987; pp 380–382.
(14) For a similar reduction of phosphine sulfides, see: Omelanczuk, J.; Perlikowska, W.; Mikolajczyk, M. *J. Chem. Soc., Chem. Commun.* **1980**, 24.
(15) Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413.

for phosphinine and 2-methylphosphinine.[16] Thus, during the conversion of 8 into 4, a migration of the ethoxycarbonyl substituent necessarily took place. Since 8 and 7 have the same stereochemistry, we explain this migration by an internal SN_2 attack of the phosphorus lone pair onto the ethoxycarbonyl-substituted carbon, leading to the selective expulsion of the trans CO_2Et substituent (eq 7).



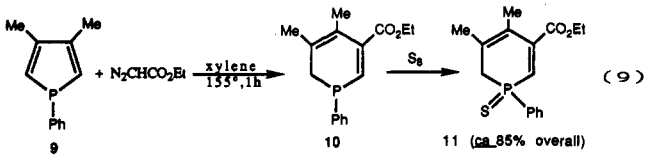
(7)

Another attractive hypothesis was suggested by one of the referees. It involves a 1,4 sigmatropic rearrangement (six electrons, with retention at the migrating carbon) to form an ylide (eq 8).



(8)

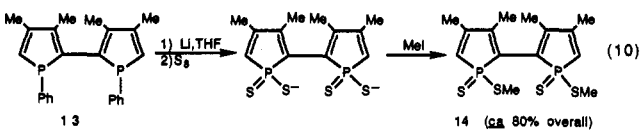
Oebels and Klamer[2] have studied the reaction of diazomethane with the tervalent phosphole 9. The reaction of 9 with ethyl diazoacetate followed an unexpected path (eq 9). The dihydrophosphinine 10 was fully characterized



(9)

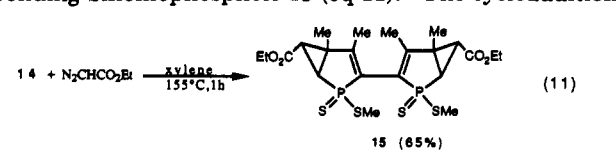
as its *P*-sulfide 11. The ethoxycarbonyl substituent is in the β position as shown by the weak coupling between the carbonyl carbon and phosphorus [δ ^{13}CO 165.6, ^3J(C–P) = 5.9 Hz]. Besides, one =CH—P and one —CH_2P group are clearly visible in the ^1H and ^{13}C NMR spectra of 11. At the moment, we have no satisfactory explanation for the formation of 10 from 9.

Having in hand a reliable two-step synthesis of 2-(ethoxycarbonyl)phosphinines from phosphole dithioesters such as 6, we decided to study its possible application to the preparation of a 2,2′-biphosphinine from a 2,2′-biphosphole. The available biphosphole 13[9] was first converted into the corresponding tetrathiodiester 14 via a classical route (eq 10). The diester 14 was obtained as



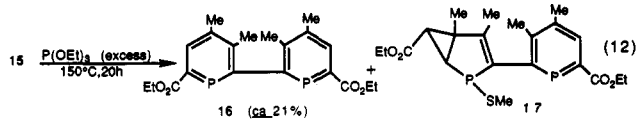
(10)

an inseparable mixture of two diastereomers. The reaction of 14 with ethyl diazoacetate then afforded the corresponding bihomophosphole 15 (eq 11). The cycloaddition



(11)

selectively takes place on the external double bonds of the two dienic systems. The ^1H and ^{13}C NMR parameters of 15 are remarkably similar to those of 7 and thus, the stereochemistry of the three-membered rings is probably identical in both cases. The two possible stereoconfigurations at the phosphorus atoms explain the presence of two diastereomers as for 14. The reduction of 15 by triethyl phosphite (triphenyl phosphite is less efficient in that case) finally gave a mixture of the expected 2,2′-biphosphinine 16 and the homophosphole–phosphinine 17 (eq 12). The formation of 17 was clearly visible in the ^{31}P



(12)

NMR spectrum of the reaction mixture [δ ^{31}P(17) +207.7 and +41.5, ^3J(P–P) = 7.3 Hz in CH_2Cl_2]. The second ring-expansion reaction appears to be more difficult than the first one and, unfortunately, limits the overall yield of biphosphinine 16. The ^1H, ^{13}C, and ^{31}P NMR parameters of 16 are remarkably similar to those of the corresponding monophosphinine 4. The most notable difference is found for the carbons at the bridge (C_2C_2') that resonate at very low field (^{13}C 168.1 ppm). Some nonbonded steric interaction between the methyl groups at C_3, C_3' probably explains their shift to higher fields [δ (MeC_3) 16.6 in 16 vs 22.2 in 4].

Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere and chromatographic separations were performed on deoxygenated silica gel columns (70–230 mesh, Merck). Coupling constants are in hertz.

2-Phenyl-4,5-dimethyl-8-(ethoxycarbonyl)-2-phospha-6,7-diazabicyclo[3.3.0]octa-3,7-diene 2-Sulfide (2). 1-Phenyl-3,4-dimethylphosphole 1-sulfide (1, 2.75 g, 1.25×10^{-2} mol) and ethyl diazoacetate (4.14 g, 3.6×10^{-2} mol) in toluene (1 mL) were allowed to stand for 45 days at room temperature. The mixture was then chromatographed with CH_2Cl_2 as eluent. Evaporation of the solvent led to 2.15 g (yield 54%) of a solid, mp 225 °C. An analytical sample was purified by crystallization from ethanol: mp 235 °C dec; ^{31}P NMR ($CDCl_3$) δ 62.3; ^1H NMR ($CDCl_3$) δ 1.30 (t, $^3J_{HH}$ = 7.1, 3 H, CH_3), 1.52 (s, 3 H, C_5-CH_3), 2.09 (q, $^4J_{HH}$ = 1.3, $^4J_{HP}$ = 2.1, 3 H, C_4-CH_3), 3.80 (d, $^2J_{HP}$ = 5.5, 1 H, C_1-H), 4.31 (q, $^3J_{HH}$ = 7.1, 2 H, OCH_2), 5.91 (dd, $^4J_{HH}$ = 1.3, $^2J_{HP}$ = 28.4, 1 H, C_3-H), 6.65 (br s, 1 H, N–H), 7.23–7.53 (m, 3 H, m and p aromatic H), 7.75–7.87 (m, 2 H, o aromatic H); ^{13}C NMR (DMSO-d_6) δ 14.57 (s, CH_3), 16.79 (d, ^3J = 17.5, C_5-CH_3), 24.19 (d, ^3J = 15.3, C_4-CH_3), 58.45 (d, ^2J = 52.2, C_1), 60.30 (s, OCH_2), 81.23 (d, ^2J = 13.4, C_5), 121.50 (d, ^1J = 80.3, C_3), 134.08 (d, ^2J = 26.7, C_8), 161.58 (d, ^2J = 22.9, C_4) 162.15 (s, CO_2), aromatic C 129.18 (d, ^3J = 12.3, meta), 131.0 (d, ^2J = 11.2, ortho), 132.32 (s, para), 133.25 (d, ^1J = 43.6, ipso); mass spectrum *m/z* (rel intensity) 334 (M^+, 85), 273 ($M^+ - N_2 - SH$, 100). Anal. Calcd for $C_{16}H_{19}N_2O_2PS$: C, 57.47; H, 5.73; N, 8.38; P, 9.26; S, 9.59. Found: C, 57.59; H, 5.77; N, 8.47; P, 9.16; S, 9.33.

2-Phenyl-4,5-dimethyl-6-(ethoxycarbonyl)-2-phosphabicyclo[3.1.0]hex-3-ene 2-Sulfide (3) A. A solution of 0.55 g (1.6×10^{-3} mol) of the diaza compound 2 in mesitylene (1 mL) was heated for 0.5 h at 160 °C. The mixture was then chromatographed twice with dichloromethane, leading to 0.35 g (yield 76%) of an oil; ^{31}P NMR (CH_2Cl_2) δ 60.5.

B. To a solution of 3.76 g (2×10^{-2} mol) of phenyldimethylphosphole sulfide 1 in 4 mL of xylene at 150 °C was added 2.75 g (2.4×10^{-2} mol) of ethyl diazoacetate in 5 min. The mixture was stirred for 1 h at 150 °C and then chromatographed, eluting with toluene and dichloromethane successively: yield 4.2 g (69%); ^{31}P NMR ($CDCl_3$) δ 59.2; ^1H NMR ($CDCl_3$) δ 1.26 (t, $^3J_{HH}$ = 7.1, 3 H, CH_3), 1.54 (s, 3 H, C_5-CH_3), 2.08 (s, 3 H, C_4-CH_3), 2.19 and 2.32 (ABX, ^3J_H = 4.9, $^3J_{HP}$ = 13.7, C_6-H; $^2J_{HP}$ = 13.0, C_1-H, 2 H), 4.14 (q, $^3J_{HH}$ = 7.1, 2 H, OCH_2), 5.40 (d, $^2J_{HP}$ = 29.5, 1 H, C_3-H), 7.52–7.83 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 12.08 (s, C_5-CH_3), 14.24 (s, CH_3), 17.55 (d, ^3J = 16.9, C_4-CH_3), 31.0 (d, ^1J = 79.3, C_1), 36.45 (d, ^2J = 2.8, C_6), 42.39 (d, ^2J = 8.4, C_5), 61.24 (s, OCH_2), 119.85 (d, ^1J = 85.5, C_3), 128.63, 131.05, 131.91 and 132.62 (aromatic C), 162.65 (d, ^2J = 13.2, C_4), 162.34 (s, CO_2); mass spectrum

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m/z (rel intensity) 306 (M^+, 70), 188 (M^+ - SCH - CO_2Et, 100). Anal. Calcd for $C_{16}H_{19}O_2PS$: C, 62.73; H, 6.25; P, 10.11; S, 10.46. Found: C, 62.92; H, 6.36; P, 9.95; S, 10.23.

2-Phenyl-4,5-dimethyl-6-(ethoxycarbonyl)-2-phosphabicyclo[3.1.0]hex-3-ene (5). To a solution of 2.6 g (8.5×10^{-3} mol) of the homophosphole sulfide **3** in THF (25 mL) was added at 0 °C 1.44 g (8.8×10^{-3} mol) of methyl trifluoromethyl sulfonate. The mixture was allowed to stand overnight at room temperature, giving a syrupy solution of the intermediate phosphonium compound (^{31}P NMR in THF δ 70.2). The mixture was cooled to about -10 °C and 0.4 g of NaH (10^{-2} mol, 60% in mineral oil) was added in three aliquots. After 1 h of stirring at room temperature, a solution of 1 mL of dry ethanol in 15 mL of toluene was slowly added. The solvents were vacuum distilled and the residue was chromatographed twice, eluting with toluene leading to 1.7 g (yield 74%) of a pale yellow oil: ^{31}P NMR ($CDCl_3$) δ -7.0; ^1H NMR ($CDCl_3$) δ 1.23 (partially masked t, $^3J_{HH}$ = 7.1, CH_3) and about 1.27 (obscured m, C_6-H; 4 H for the two signals), 1.49 (s, 3 H, C_5-CH_3), 2.01 (dd, $^4J_{HP}$ = 1.4, $^4J_{HH}$ = 1.3, 3 H, C_4-CH_3), 2.16 (ddd, $^2J_{HP}$ = 12.2, $^3J_{HH}$ = 5.2, $^4J_{HH}$ = 1.8), 4.11 (ABX, 2 H, OCH_2), 5.52 (dm, $^2J_{HP}$ = 41.7, $^4J_{HH}$ = 1.3, C_3-H), 7.22-7.44 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 13.22 (s, C_5-CH_3), 14.16 (s, CH_3), 17.37 (d, ^3J = 2.5, C_4-CH_3), 34.66 (d, ^1J = 10.6, C_1), 35.01 (d, ^2J = 10.1, C_6), 44.26 (d, ^2J = 7.5, C_5), 60.3 (s, OCH_2), 122.86 (d, ^1J = 13.8, C_3), 156.69 (s, C_4), 170.27 (s, CO_2), aromatic C 128.20 (d, J = 6.8, meta), 129.16 (s, para), 132.55 (d, J = 20.0, ortho), 137.59 (d, J = 19.6, ipso); mass spectrum m/z (relative intensity) 274 (M^+, 30), 201 (M^+ - CO_2Et, 100). A sample of the homophosphole **5** was reconverted to its sulfide **3** by heating for 10 min at 50 °C with 1 equiv of sulfur in toluene; yield 85%.

4,5-Dimethyl-2-(ethoxycarbonyl)phosphinine (4) A. A mixture of 4.45 g (1.6×10^{-2} mol) of the homophosphole **5** or 5.0 g (1.6×10^{-2} mol) of its sulfide **3** and 5.0 g of Ni powder on 10 g silica in mesitylene (15 mL) was heated for 20 h at 170-180 °C. The reaction mixture was chromatographed, eluting with toluene, leading to 1.5-1.6 g of an oil containing the homophosphole (**5**, ^{31}P NMR in toluene, δ -5.2), the phosphinine (**4**, δ ^{31}P 205.8) in about the same proportions, and two or three very minor products. This mixture was heated for 5 min at 50 °C with 0.2 g of elemental sulfur to convert the homophosphole **5** into its sulfide. Chromatography of the reaction mixture first with hexane to elute the excess of sulfur and then with hexane-toluene 1/1 led to 0.5 g of a pale yellow oil; ^{31}P NMR ($CDCl_3$) δ 202.8.

B. A solution of 3.6 g (1.3×10^{-2} mol) of the *P*-methylthio homophosphole sulfide **7** and 8.1 g (2.6×10^{-2} mol) of triphenyl phosphite were heated for 20 h at 160 °C. The reaction mixture was then chromatographed first with hexane-20% toluene to eliminate the phosphite sulfide and then with toluene: yield 1.9 g (76%) of a pale yellow oil; ^{31}P NMR ($CDCl_3$) 202.5. Further purification of an analytical sample was performed by distillation in a Kugelrohr apparatus at 160-5 °C under 1.5 mm/Hg: ^1H NMR ($CDCl_3$) δ 1.40 (t, $^3J_{HH}$ = 7.1, 3 H, CH_3), 2.38 (d, $^4J_{HP}$ = 3.5, 3 H, C_5-CH_3), 2.4 (s, 3 H, C_4-CH_3), 4.40 (q, $^3J_{HH}$ = 7.1, 2 H, OCH_2), 8.40 (d, $^3J_{HP}$ = 3.5, C_3-H), 8.50 (d, $^2J_{HP}$ = 39.7, C_6-H, 2 H for the two signals); ^{13}C NMR ($CDCl_3$) δ 14.40 (s, CH_3), 22.18 (s, C_4-CH_3), 23.44 (d, ^3J = 2.7, C_5-CH_3), 61.30 (s, OCH_2), 139.02 (s, C_4), 139.43 (d, ^2J = 13.9, C_3), 146.95 (d, ^3J = 13.7, C_5), 154.44 (d, ^1J = 48.3, C_2), 155.23 (d, ^1J = 49.7, C_6), 168.25 (d, ^2J = 24.6, CO_2); mass spectrum m/z (rel intensity) 196 (M^+, 45). Anal. Calcd for $C_{10}H_{13}O_2P$: C, 61.22; H, 6.68; P, 15.79. Found: C, 61.31; H, 6.86; P, 15.62.

The P^{III} compound **8** heated under the same conditions with 1 equiv of triphenyl phosphite gave the same results. The phosphinine was also obtained by heating the homophosphole sulfide **7** with zinc amalgam in mesitylene (15 h at 170 °C; yield 60%) or with Ni powder on silica (lower yield).

2-(Methylthio)-4,5-dimethyl-6-(ethoxycarbonyl)-2-phosphabicyclo[3.1.0]hex-3-ene 2-Sulfide (7). To a solution of 5.7 g (3×10^{-2} mol) of the (methylthio)phosphole sulfide **6** in 15 mL of xylene at 145 °C was added in 10-15 min 4.1 g (3.6×10^{-2} mol) of ethyl diazoacetate. The mixture was stirred for 1 h at the same temperature and then chromatographed. After elimination of byproducts with toluene, the homophosphole sulfide was eluted with a mixture of dichloromethane and toluene (80/20): white solid; yield 6.5 g (78%); mp 120 °C; ^1H NMR ($CDCl_3$) δ 1.29 (t, $^1J_{HH}$ = 7.1, 3 H, CH_3), 1.47 (s, 3 H, C_5-CH_3), 2.05 (pseudo t, 3 H, C_4-CH_3), 2.15 and 2.37 (ABX; A part, dd, $^3J_{AB}$ = 4.9, $^2J_{BX}$ = 13.5, 1 H, C_6-H; B part, dd, $^3J_{BX}$ = 12.8, 1 H, C_1-H), 2.29 (d, $^3J_{HP}$ = 14.3, 3 H, SCH_3), 4.14 and 4.20 (ABX_3, $^2J_{AB}$ = 10.7, $^3J_{AX}$ and $^3J_{BX}$ = 7.1, 2 H, OCH_2), 5.40 (d, $^2J_{HP}$ = 31.1, C_3-H); ^{13}C NMR ($CDCl_3$) δ 11.85 (d, ^3J = 2.1, C_5-CH_3), 14.20 (s, CH_3), 14.40 (d, ^2J = 4.5, SCH_3), 17.50 (d, ^3J = 18.3, C_4-CH_3), 32.65 (d, ^1J = 76.9, C_1), 37.40 (d, ^2J = 4.5, C_6), 41.33 (s, C_5), 61.34 (s, OCH_2), 119.29 (d, ^1J = 85.0, C_3), 162.70 (d, ^2J = 15.9, C_4), 167.70 (d, ^3J = 2.9, CO_2); mass spectrum m/z (rel intensity) 276 (M^+, 60), 171 (M^+ - S - CO_2Et, 100). Anal. Calcd for $C_{11}H_{17}O_2PS_2$: C, 47.81; H, 6.20; P, 11.21. Found: C, 47.96; H, 6.20; P, 11.12.

2-(Methylthio)-4,5-dimethyl-6-(ethoxycarbonyl)-2-phosphabicyclo[3.1.0]hex-3-ene (8) was prepared under the same conditions as the homophosphole **5**: yield 83%; pale yellow oil; ^{31}P NMR (CH_2Cl_2) δ 29.3; ^1H NMR ($CDCl_3$) δ 1.16 and 2.25 (ABX; A part, dd, $^3J_{HH}$ = 5.1, $^3J_{HP}$ = 4.2, 1 H, C_6-H; B part, $^3J_{HH}$ = 5.1, $^2J_{HP}$ = 12.6, 1 H, C_1-H), 1.26 (t, $^3J_{HH}$ = 7.1, 3 H, CH_3), 1.45 (s, 3 H, C_5-CH_3), 1.91 (d, $^3J_{HP}$ = 4.1, 3 H, SCH_3), 2.0 (dd, $^4J_{HP}$ = 2.7, $^4J_{HH}$ = 1.3, 3 H, C_4-CH_3), 4.13 (ABX_3, 2 H, OCH_2), 5.32 (dd, $^2J_{HP}$ = 43.9, $^4J_{HH}$ = 1.3, 1 H, C_3-H); ^{13}C NMR ($CDCl_3$) δ 11.35 (d, ^2J = 12.8, SCH_3), 12.16 (s, C_5-CH_3), 14.25 (s, CH_3), 17.18 (s, C_4-CH_3), 34.95 (d, ^1J = 24.4, C_1), 36.22 (d, ^2J = 10.9, C_6), 43.74 (d, ^2J = 8.4, C_5), 60.51 (s, OCH_2), 119.54 (d, ^1J = 25.2, C_3), 158.21 (s, C_5), 169.11 (s, CO_2); mass spectrum m/z (rel intensity) 244 (M^+, 15), 171 (M^+ - CO_2Et, 100). A sample of the homophosphole **8** was reconverted to its sulfide **7** by heating with 1 equiv of sulfur in toluene: yield 90%; mixed melting point with an authentic sample of **7**, 119 °C. The compound **8** was also prepared by heating its sulfide **7** for 1 h in refluxing toluene with 1.2 equiv of tributylphosphine. The crude product needed to be chromatographed three times and the yield was about 70%.

4,5-Dimethyl-3-(ethoxycarbonyl)-1-phenyl-1,6-dihydrophosphinine (10) and 1-Sulfide (11). To a solution of 5.0 g (2.65 $\times 10^{-2}$ mol) of dimethylphenylphosphole **9** in xylene (6 mL) at 155 °C was added in 5-10 min 3.63 g (3.2×10^{-2} mol) of ethyl diazoacetate. The mixture was stirred for 1 h at the same temperature. After cooling, the solution was chromatographed, eluting with toluene leading to 5.8 g of an impure oil, which could not be purified, decomposition occuring on the column: ^{31}P NMR ($CDCl_3$) δ -11.4; ^1H NMR selected data ($CDCl_3$) δ 1.08 (t, $^3J_{HH}$ = 7.1, 3 H, CH_3), 2.05 (d, J_{HH} = 3.2) and 2.09 (d, J_{HP} = 3.3, 6 H, C_4 and C_5-CH_3), 2.43 and 2.65 (ABX, $^2J_{HH}$ = 13.1, $^2J_{HP}$ = 5.5, 2 H, C_6-H_2), 3.85 (q, $^3J_{HH}$ = 7.1, 2 H, OCH_2), 6.35 (d, $^2J_{HP}$ = 39.6, 1 H, C_2-H), 7.15-7.35 (m, 5 H, C_6H_5).

Sulfide 11. A sample of the impure dihydrophosphinine **10** was heated for 10 mn at 50 °C with about 2 equiv of elemental sulfur in toluene. The reaction mixture was then chromatographed first with hexane-toluene (1/1) and then with toluene-dichloromethane (1/1): yield 80-85% of an oil; ^{3P} NMR ($CDCl_3$) δ 44.9; ^1H NMR ($CDCl_3$) δ 1.19 (t, $^3J_{HH}$ = 7.1, 3 H, CH_3), 1.99 (d, $^4J_{HP}$ = 2.5, 3 H, C_5-CH_3), 2.12 (s, 3 H, C_4-CH_3), 3.01 and 3.09 (ABX; A part, $^2J_{HH}$ = 13.5, $^2J_{HP}$ = 14.6; B part, $^2J_{HH}$ = 13.5, $^2J_{HP}$ = 14.8, 2 H, C_6-H_2), 4.08 (q, $^3J_{HH}$ = 7.1, 2 H, OCH_2), 6.15 (d, $^2J_{HP}$ = 31.2, 1 H, C_2-H), 7.34-7.58 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 14.23 (s, CH_3), 14.56 (s, C_4-CH_3), 18.0 (d, ^3J = 17.9, C_5-CH_3), 40.6 (d, ^1J = 40.1, C_6), 61.47 (s, OCH_2), 121.0 (d, ^2J = 82.0, C_1), 132.61 (d, ^2J = 12.7, C_3), 146.66 (d, ^2J = 27.2, C_5), 154.41 (d, ^3J = 18.6, C_4-CH_3), 165.6 (d, ^3J = 5.9, CO_2), aromatic C 128.3 (s, para), 128.6 (s, meta), 129.2 (d, J = 4.0, ortho) and 134.2 (d, J = 79.0, ipso); mass spectrum m/z (rel intensity) 306 (M^+, 40). Anal. Calcd for $C_{16}H_{19}O_2PS$: C, 62.73; H, 6.25; P, 10.11; S, 10.46. Found: C, 62.98; H, 6.40; P, 10.12; S, 10.25.

3,3',4,4'-Tetramethyl-1,1'-bis(methylthio)-2,2'-biphospholyl 1,1'-Disulfide (14). To a solution of 3.5 g (9.3×10^{-3} mol) of diphosphole **13** in dry THF (75 mL) was added at 0 °C about 0.4 g of Li. After the mixture was stirred for 3 h at room temperature, excess Li was removed by filtration through glass wool and 0.45 g of anhydrous $AlCl_3$ and 0.88 g of *t*-BuCl were successively added at -10 °C. The reaction mixture was stirred for 0.5 h at the same temperature, and then 1.2 g (4.7×10^{-3} mol) of S_8 was rapidly added. The mixture was stirred for 30 min to complete the formation of the dithioanion (δ ^{31}P 69.5, single signal) and then 2.7 g (1.9×10^{-2} mol) of methyl iodide was added. After 30 min of stirring at room temperature, the solvent was removed under vacuum and the residue chromatographed first with toluene and then with dichloromethane: yield 2.8 g (80%) of a mixture of two

diastereoisomers; mp about 200 °C; ^{31}P NMR (THF) δ 67.2 and 67.7; ^1H NMR ($CDCl_3$) δ 1.96 (m, $^5J_{HH}$ = 0.5, 1.35 H, C_3-CH_3 A isomer), 2.03 (m, $^5J_{HH}$ = 0.5, 1.65 H, C_3-CH_3 B isomer), 2.12 (m, $^4J_{HP}$ = 1.7) and 2.15 (m, $^4J_{HP}$ = 1.7, 3 H; C_4-CH_3 A and B), 2.27 (d, $^2J_{HP}$ = 14.6, 1.65 H, SCH_3 B), 2.37 (d, $^2J_{HP}$ = 14.9, 1.35 H, SCH_3 A), 6.02 (dm, $^2J_{HP}$ = 33.5, $^5J_{HH}$ = 0.5, 0.55, C_5-H B), 6.14 (dm, $^2J_{HP}$ = 33.4, 0.45 H, C_5-H A); ^{13}C NMR selected data ($CDCl_3$) δ 13.08 (s, CH_3), 15.21 (d, ^2J = 14.1) and 17.46 (d, ^2J = 18.1, SCH_3 A and B), 125.02 (pseudo t, ^2J = 84.4, C_5), 149.88 and 151.45 (m, C_5 A and B); mass spectrum m/z (rel intensity) 378 (M^+, 70), 331 (M^+ - SMe, 100), 299 (M^+ - SMe - S, 50), 220 (M^+ - 2SMe - 2S, 50). Anal. Calcd for $C_{14}H_{20}P_2S_4$: C, 44.43; H, 5.33; P, 16.36; S, 33.88. Found: C, 44.67; H, 5.30; P, 15.98; S, 34.03.

4,4',5,5'-Tetramethyl-2,2'-bis(methylthio)-6,6'-bis(ethoxycarbonyl)-2,2'-diphospha-3,3'-bi[bicyclo[3.1.0]hex-3-enyl] 2,2'-Disulfide (15). To a solution of 2.0 g (5.3 × 10^{-3} mol) of diphosphole disulfide 14 in xylene (10 mL) at 150 °C was added 1.52 g (1.33 × 10^{-2} mol) of ethyl diazoacetate over 10 min. The mixture was stirred for 1 h at 150 °C and then chromatographed first with dichloromethane and then with dichloromethane/ethyl acetate (80-20): yield 1.8 g (62%); mixture of two isomers; ^{31}P NMR (xylene) δ 81.6 and 81.9. An analytical sample was recrystallized in dichloromethane, leading to one of the diastereoisomers: mp 224 °C; ^{31}P NMR ($CDCl_3$) δ 80.5; ^1H NMR ($CDCl_3$) δ 1.31 (t, $^3J_{HH}$ = 7.1, CH_3), 1.55 (s, 3 H, C_5-CH_3), 1.92 (pseudo t, 3 H, C_4-CH_3), 2.30 (d, $^3J_{HP}$ = 14.4, SCH_3), 2.05 and 2.46 (ABX; A part, dd, $^3J_{HH}$ = 4.7, $^3J_{HP}$ = 13.2, 1 H, C_6-H; B part, dd, $^3J_{HH}$ = 4.7, $^2J_{HP}$ = 12.5, 1 H, C_1-H), 4.20 (ABX_3, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 12.28 (s, S-CH_3), 14.25 (s, CH_3), 15.86 (s, C_5-SCH_3), 16.40 (d, ^3J = 13.4, C_4-CH_3), 31.79 (d, ^1J = 77.3, C_1), 37.55 (s, C_6), 41.20 (d, ^2J = 3.6, C_5), 61.66 (s, OCH_2), 121.0 (dd, ^1J = 82.7, ^2J = 13.7, C_3), 162.45 (dd, ^2J = 25.4, ^3J = 6.1, C_4), 167.58 (s, CO_2); mass spectrum m/z (rel intensity) 550 (M^+, 75), 503 (M^+ - SMe, 100). Anal. Calcd for $C_{22}H_{32}O_4P_2S_4$: C, 47.98; H, 5.86; P, 11.25; S, 23.29. Found: C, 47.73; H, 5.95; P, 10.96; S, 23.31.

3,3',4,4'-Tetramethyl-6,6'-bis(ethoxycarbonyl)-2,2'-biphosphinine (16). A mixture of 2.0 g (3.6 × 10^{-3} mol) of the bis homophosphole sulfide 15 and 2.4 g (1.44 g × 10^{-2} mol) of triethyl phosphite was heated for 20 h at 150 °C. After cooling, the residue was twice chromatographed with toluene, leading to 0.85 g of a mixture of two products: the biphosphinine 16, δ ^{31}P (CH_2Cl_2) 202.9, and the homophosphole-phosphinine 17, δ ^{31}P (CH_2Cl_2) 207.7 (d) and 41.8 (d), $^3J_{PP}$ = 7.3 Hz. This mixture was once more chromatographed with toluene, giving first 0.3 g (yield 21.5%) of the biphosphinine 16 [^{31}P NMR ($CDCl_3$) δ 202.6; ^1H NMR ($CDCl_3$) δ 1.40 (t, $^3J_{HH}$ = 7.1, 6 H, CH_3), 2.12 (s, 6 H, C_3-CH_3), 2.50 (s, 6 H, C_4-CH_3), 4.41 (q, $^3J_{HH}$ = 7.1, 4 H, OCH_2), 8.45 (s, 2 H, C_5-H); ^{13}C NMR ($CDCl_3$) δ 14.35 (s, CH_3), 16.61 (s, C_3-CH_3), 23.35 (s, C_4-CH_3), 61.47 (s, OCH_2), 138.54 (pseudo t, C_5), 140.42 (pseudo t, C_3), 144.97 (s, C_4), 153.90 (AXX', ^1J = 53.5, C_6), 168.10 (pseudo t, C_2), 172.10 (AXX', ^2J = 21.4, CO_2); mass spectrum m/z (rel intensity) 390 (M^+, 100). Anal. Calcd for $C_{20}H_{24}O_4P_2$: C, 61.54; H, 6.20; P, 15.87. Found: C, 61.80; H, 6.39; P, 15.55.] and then 0.2 g of a mixture of about 30% of the biphosphinine 16 and 70% of the compound 17 [^1H NMR ($CDCl_3$) δ 8.35 (d, ^3J = 4.3, 0.55 H, 17 C_5-H), 8.44 (s, 0.45 H, 16 C_5-H); mass spectrum m/z (rel intensity) 438 (17 M^+, 70), 390 (16 M^+, 100), 365 (17 M^+ - CO_2Et, 90), 317 (16 M^+ - CO_2Et, 30)].

Supplementary Material Available: Structural report for 7, including a description of data collection, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

Nickel-Catalyzed Olefination of Cyclic Benzylic Dithioacetals by Grignard Reagents. Scope and Mechanism[1]

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The details of the first nickel-catalyzed olefination of cyclic dithioacetals to form substituted styrenes and aryl-substituted 1,4-pentadienes are described. The reaction represents a new synthetic use of the dithioacetal functionality. Only nickel complexes catalyzed these cross-coupling reactions; palladium complexes displayed no catalytic activity under the reaction conditions employed. Selective coupling occurred. A mechanism for the reaction is proposed. The experimental evidence indicates that, in these nickel-catalyzed couplings, cyclic dithioacetals are more reactive than their acyclic analogues. This increased reactivity appears to be the result of maintaining the two sulfur atoms in close proximity to each other by the use of a short chain of methylene groups.

The dithioacetal functionality was first described in 1885.[3] Since that time it has come to be considered a latent carbonyl or methylene group.[4,5] However, reports of the transformation of the dithioacetal functionality to other functional groups have been few.[6-8] In general, the dithioacetal functionality is relatively stable toward nu-

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