[6.1.0]nonane, 286-60-2; indene, 95-13-6; cycloprop[a]indene, 15677-15-3; 2-carene, 554-61-0; 3,3,7-trimethyltricyclo-[5.1.0.0^{2,4}]octane, 33046-07-0; 3-carene, 13466-78-9; 1,4,4-trimethyltricyclo[5.1.0.0^{3,5}]octane, 125495-68-3; α-pinene, 80-56-8; 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane, 32549-17-0; β-pinene, 127-91-3; 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1′-cyclopropane], 35117-81-8; crotyl alcohol, 6117-91-5; 1-(hydroxymethyl)-2-methylcyclopropane, 6077-72-1; 3,4-dihydro-2*H*-pyran, 110-87-2; 2-oxabicyclo[4.1.0]heptane, 286-16-8; (1-cyclohexenyloxy)trimethylsilane, 6651-36-1; 1-(trimethylsiloxy)bicyclo-[4.1.0]heptane, 38858-74-1; 1-pyrrolidino-1-cyclohexene, 1125-99-1; 1-pyrrolidinobicyclo[4.1.0]heptane, 4668-96-6.

Arylation and Heteroarylation of the Phosphole Ring

Eliane Deschamps and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

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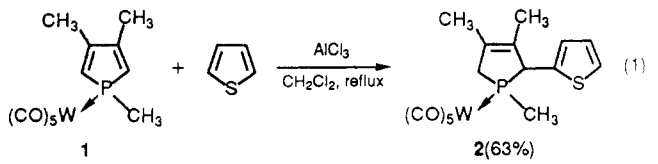
In the presence of $AlCl_3$, the dienic system of a phosphole P–$W(CO)_5$ complex can serve to alkylate electron-rich arenes such as anisole or heteroarenes such as furan and thiophene. The 2-aryl-2,5-dihydrophosphole complexes thus obtained can be converted into the corresponding 2-arylphospholes via decomplexation, reduction, bromination, and dehydrobromination. The overall yields are satisfactory. The thiophene ring can serve as a functionalizable carrier for the phosphole ring. Thus, a 2-(2-thienyl)phosphole P–$W(CO)_5$ complex can be easily acetylated or formylated on the C_5 position of the thiophene ring by CH_3 C(O)Cl + $AlCl_3$ or HC(O)N(Me)Ph + PO Cl_3, respectively.

Contrary to the analogous pyrrole, furan, and thiophene rings, the phosphole ring is almost totally devoid of aromatic chemistry. The nonplanarity of the phosphorus atom prevents the full delocalization of the electronic sextet.[1] As a consequence, it is quite difficult to functionalize a phosphole[2] or to couple it with other preformed structures contrary to its nitrogen, oxygen, and sulfur counterparts. In view of that situation, we thought that it would be interesting to graft a phosphole onto an aromatic heterocycle which, then, could act as a "carrier" for the phosphorus heterocycle. We describe here how it is possible to link a phosphole with a furan or a thiophene ring and how it is possible to functionalize the sulfur heterocycle without destroying the bonded phosphole unit.

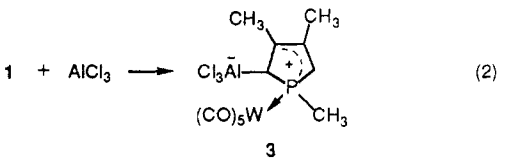
Results and Discussion

Our starting point was a previous observation[3] concerning the possible use of the dienic system of a phosphole complex as alkylating agent for a thiophene ring (eq 1).



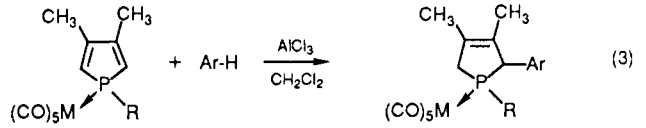
(1)

The reaction mechanism probably involves a zwitterionic complex **3** between $AlCl_3$ and the dienic system which is able to act as an electrophile toward the thiophene ring (eq 2). Indeed, when $AlCl_3$ is mixed with **1** in CH_2Cl_2 solution, complex **1** (δ ^{31}P −8.2 ppm vs H_3PO_4) disappears and a new product is formed (δ ^{31}P −23.9 ppm). Upon subsequent addition of water, this new product is destroyed and the initial complex **1** is reformed.



(2)

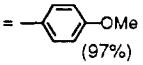
While this reaction gives a single isomer, its stereochemistry could not be assigned with certainty. The α-C*H* Ar ring proton shows no coupling with phosphorus, but we cannot transpose to phospholene complexes the relationship between the H–C–P lone pair dihedral angle and ^2J(H–P) coupling constant which was established for the corresponding free phosphines.[4] As a first step, we decided to check the generality of this coupling reaction. It soon appeared that it could be generalized to electron-rich arenes such as anisole and to furan (eq 3).



(3)

4: R = Ph; M = W
5: R = Ph; M = Mo
6: R = Me; M = Mo

7: R = Ph; M = W; Ar =  (60%)

8: R = Ph; M = Mo; Ar =  (97%)

9: R = Me; M = Mo; Ar =  (76%)

On the contrary, a normal arene such as toluene failed to react and pyrroles gave intractable products. It clearly appears that zwitterions such as **3** are relatively weak electrophiles. In each cases, the final products **7**–**9** are pure

(1) The chemistry of phospholes has been recently reviewed. The review includes a discussion on phosphole aromaticity: Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

(2) A few functional phospholes have been described in the literature but no general method is available for their synthesis: Quin, L. D.; Borleske, S. G. *Tetrahedron Lett.* **1972**, 299. Mathey, F. *Tetrahedron* **1976**, *32*, 2395. Santini, C. C.; Mathey, F. *J. Org. Chem.* **1985**, *50*, 467. Marinetti, A.; Mathey, F. *Tetrahedron Lett.* **1987**, *28*, 5021. Wai Hé-Line, Wai Tan; Foucaud, A. *Tetrahedron Lett.* **1988**, *29*, 4581.

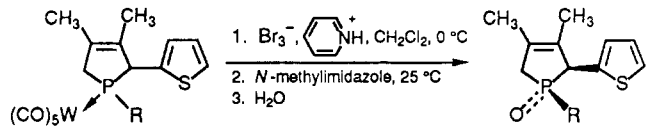
(3) Deschamps, E.; Mathey, F. *J. Organomet. Chem.* **1987**, *332*, 141.

(4) Albrand, J. P.; Martin, J.; Robert, J. B. *Bull. Soc. Chim. Fr.* **1969**, 40.

0022-3263/90/1955-2494$02.50/0

isomers showing the same absence of $^2J(P\text{–}CH\ Ar)$ coupling as already noted for **2**.

As a second step, we investigated the decomplexation of the arene–5-substituted complexes **2**, **7**–**9**. The decomplexation of the tungsten derivatives **2** and **7** was performed using an already well documented technique.[5] Tungsten(0) is first converted into tungsten(II) by bromination with pyridinium perbromide and, then, the weakened P–W bond is broken using a nitrogen ligand such as *N*-methylimidazole (eq 4).

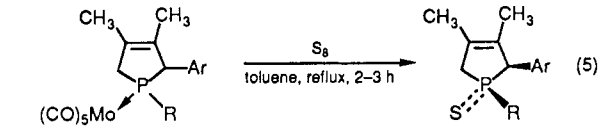


2: R = Me
7: R = Ph

10: R = Me (~50%)
11: R = Ph (~60%)

(4)

The decomplexation of the molybdenum derivatives **8** and **9** was performed by reaction with sulfur[6] (eq 5).



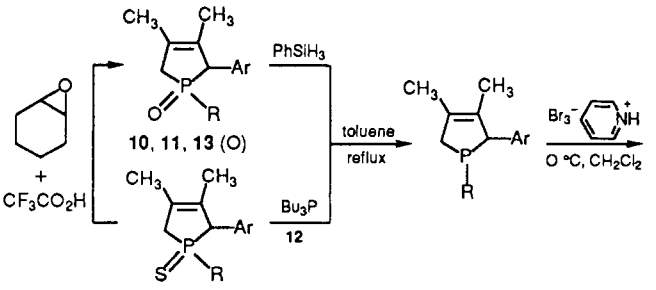
8: R = Ph; Ar = OMe
9: R = Me; Ar =

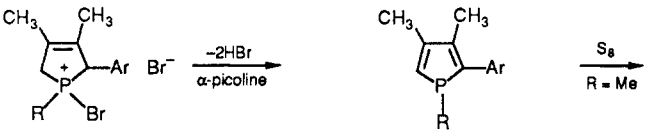
12 (70%)
13 (75%)

(5)

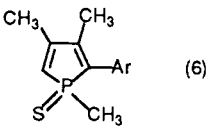
All the products **10**–**13** thus obtained display a strong $^2J(P\text{–}CHAr)$ coupling constant (between 15.7 Hz for **13** and 19.8 Hz for **11**). According to the data of the literature,[7] this result unambiguously demonstrates that the corresponding protons are cis to the P=O or P=S groups. However, since we are not sure whether or not the decomplexation takes place with retention of the configuration at phosphorus, we cannot tell anything more concerning the stereochemistry of the initial coupling reaction. The conversion of phospholene oxides **10**, **11** or sulfides **12**, **13** into the corresponding phospholes then followed a well-established path.[1] These species were first reduced either by $PhSiH_3$ or Bu_3P, respectively, and then brominated at P and, finally, dehydrobrominated by a tertiary amine (eq 6).

The various steps were monitored by ^{31}P NMR spectroscopy, and the intermediate products were used without complete purification. The last step followed an optimized procedure which had been thoroughly described.[8] The two 1-methylphospholes **15** and **17** were characterized as their *P*-sulfides **18** and **19** because they are far too sensitive toward oxidation. Having in hands these new arylated phospholes, the last point which remained to be checked concerned the possible use of the arene or heteroarene rings of **14**–**17** as functionalizable "carriers". The experiments were performed with the 2-thienylphosphole **14**. As





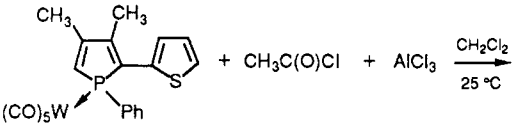
14: R = Ph; Ar = (70% overall)
15: R = Me; Ar =
16: R = Ph; Ar = OMe (70%)
17: R = Me; Ar =



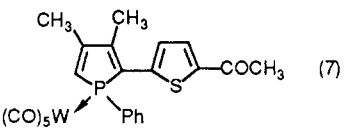
(6)

18: Ar =
19: Ar = (50%)

for the arylation of the phosphole ring, it is, of course, necessary to protect the lone pair at phosphorus before any functionalization attempt. Since oxidation leads to phosphole oxide [4 + 2] dimers,[1] and since phosphole sulfides are attacked at sulfur by $AlCl_3$,[9] the only efficient protection is, once again, complexation. As previously, we selected the highly resistant $W(CO)_5$ complexing group. We easily performed the acetylation (eq 7) and the formylation (eq 8) of the phosphole complex **20** using the standard conditions.



20



(7)

21 (~100%)

Selected synthetic uses of these arylation and functionalization techniques will be described in due course.

Experimental Section

All reactions were performed under argon. NMR spectra were recorded on multinuclear WP 80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 (^1H), 20.15 and 50.32 (^{13}C), and 32.44 (^{31}P) MHz. Chemical shifts are in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in hertz. Mass spectra were recorded

(5) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 45. Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001. Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791. Deschamps, B.; Mathey, F. *New J. Chem.* **1988**, *12*, 755.

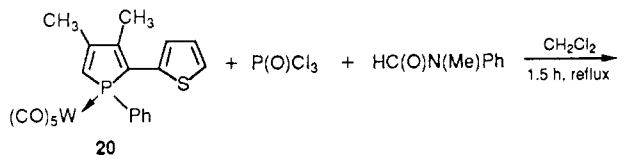
(6) The decomplexation of $R_3P\text{–}Mo(CO)_5$ complexes by reaction with sulfur has already been described in some particular cases, see: Santini, C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.

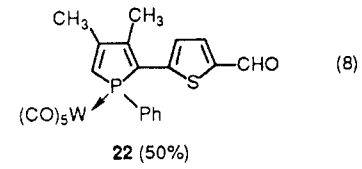
(7) Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; pp 380–381.

(8) Brêque, A.; Mathey, F.; Savignac, Ph. *Synthesis* **1981**, 983.

(9) Deschamps, E., Unpublished results.

(10) Alcaraz, J. M.; Mathey, F. *Tetrahedron Lett.* **1984**, *25*, 4659.





(8)

on a Shimadzu GC–MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France. All the new products gave correct C, H elemental analyses except the oxides **10** and **11** and the sulfide **13**, which tenaciously retain solvents. Silica gel (70–230 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers. The experiments were carried out under argon.

[1-Phenyl-2-(2-thienyl)-3,4-dimethyl-2,5-dihydrophosphole]pentacarbonyltungsten (7). Complex **4**[6] (20.5 g, 4×10^{-2} mol), thiophene (6.4 mL, 8×10^{-2} mol), and $AlCl_3$ (5.9 g, 4.4×10^{-2} mol) were allowed to react for 10 min in dry CH_2Cl_2 (80 mL). The solution became deep purple. Then, the reaction mixture was slowly poured onto a saturated aqueous solution of NH_4Cl mixed with powdered ice. The organic phase became deep yellow. The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with water until neutrality. After drying ($MgSO_4$) and evaporation of CH_2Cl_2, the organic residue was chromatographed with hexane/ether, 95/5, as the eluent. Yield: ca. 14 g of white crystals (~60%). ^{31}P NMR (CH_2Cl_2): δ +14.2 ppm, $^1J(^{31}P-^{183}W)$ 236.8 Hz. ^1H NMR (C_6D_6): δ 1.48 (s, 3 H, Me), 1.60 (s, 3 H, Me), 2.73 (broad d, $^2J(H-H) \sim$ 14 Hz, $^2J(H-P) \sim 0$ Hz, 1 H, CH_2), 3.28 (pseudo t, $^2J(H-H) \sim {}^2J(H-P) \sim$ 14 Hz, 1 H, CH_2), 4.61 (s, 1 H, P-CH), 6.21, 6.41, and 6.53 (3 m, 3 × 1 H, CH thiophene), 6.90 (m, 3 H, Ph meta + para), 7.08 (m, 2 H, Ph ortho). ^{13}C NMR (C_6D_6): δ 14.57 (d, $^3J(C-P)$ = 6 Hz, Me), 16.36 (d, $^3J(C-P)$ = 7.6 Hz, Me), 39.56 (d, $^1J(C-P)$ = 27.7 Hz, CH_2-P), 58.92 (d, $^1J(C-P)$ = 22.8 Hz, CH-P), 197.37 (d, $^2J(C-P)$ = 6.9 Hz, cis CO), 199.50 (d, $^2J(C-P)$ = 22.3 Hz, trans CO). Mass spectrum (^{184}W): m/z 596 (M^+, 30), 568 ($M^+ - CO$, 21), 512 ($M^+ - 3CO$, 80), 456 ($M^+ - 5CO$, 100). Anal. Calcd for $C_{21}H_{17}O_5PSW$: C, 42.28; H, 2.85. Found: C, 42.28; H, 2.60.

[1-Phenyl-2-(*p*-methoxyphenyl)-3,4-dimethyl-2,5-dihydrophosphole]pentacarbonylmolybdenum (8). The same experimental procedure as for **7** was used. Starting with complex **5**[6] (4.24 g, 1×10^{-2} mol), anisole (1.1 mL, 1.1×10^{-2} mol), and $AlCl_3$ (1.5 g, 1.1×10^{-2} mol), 5.16 g (97%) of a colorless oil was obtained after chromatography with hexane/ether, 90/10, as the eluent. ^{31}P NMR (CH_2Cl_2): δ +32 ppm. ^1H NMR ($CDCl_3$): δ 1.55 (s, 3 H, Me), 1.95 (s, 3 H, Me), 3.0 (m, 1 H, CH_2), 3.45 (m, 1 H, CH_2), 3.65 (s, 3 H, OMe), 4.3 (broad s, 1 H, CH-P), 6.51 (pseudo s, 4 H, anisole), 7.10 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.74 (d, $^3J(C-P)$ = 5 Hz, Me), 16.83 (d, $^3J(C-P)$ = 6 Hz, Me), 39.98 (d, $^1J(C-P)$ = 23 Hz, CH_2-P), 55.21 (s, OMe), 62.91 (d, $^1J(C-P)$ = 18 Hz, CH-P), 158.48 (s, *C*-OMe), 205.98 (d, $^2J(C-P)$ = 9 Hz, cis CO). Mass spectrum (^{98}Mo): m/z 534 (M^+, 19), 393 ($M^+ - 5CO - H$, 100). Anal. Calcd for $C_{24}H_{21}MoO_6P$: C, 54.14; H, 3.95. Found: C, 54.67; H, 4.25. Complex **8** is contaminated by variable amounts of the corresponding trans $L_2Mo(CO)_4$ complex. ^{31}P NMR: δ +54 ppm. ^{13}C NMR: δ 217.0 (d, $^2J(C-P)$ = 13 Hz, $Mo(CO)_4$). This explains the rather high results for C and H. We have often noticed that $AlCl_3$ catalyzes the dismutation of L $Mo(CO)_5$ complexes.

[2-(2-Furyl)-1,3,4-trimethyl-2,5-dihydrophosphole]pentacarbonylmolybdenum (9). Complex **6** (3.62 g, 1×10^{-2} mol) and $AlCl_3$ (1.5 g, 1×10^{-2} mol) were stirred at room temperature in CH_2Cl_2 (20 mL) for 20 min. The resulting mixture was added dropwise to furan (3.5 mL, 5×10^{-2} mol) in CH_2Cl_2 (5 mL). After 30 min, the reaction mixture was hydrolyzed and further treated as in the case of **7**; 3.3 g (76%) of a colorless oil was obtained after chromatography with hexane as the eluent. ^{31}P NMR (CH_2Cl_2): δ ^{31}P 20.9 ppm. ^1H NMR ($CDCl_3$): δ 1.15 (d, $^2J(H-P)$ = 6.4 Hz, 3 H, Me-P), 1.66 (s, 3 H, Me-C), 1.82 (s, 3 H, Me-C), 2.69 (m, 2 H, CH_2-P), 4.24 (broad s, 1 H, CH-P), 6.12 (m, 1 H, Hβ furan), 6.34 (m, 1 H, Hβ furan), 7.35 (m, 1 H, Hα furan). ^{13}C NMR ($CDCl_3$): δ 14.58 (d, $^3J(C-P)$ = 5.1 Hz, *Me*-C), 15.19 (d, $^1J(C-P)$ = 18.8 Hz, (Me-P), 16.80 (d, $^3J(C-P)$ = 6.3 Hz, *Me*-C), 42.20 (d, $^1J(C-P)$ = 22.4 Hz, CH_2-P), 54.30 (d, $^1J(C-P)$ = 21.3 Hz, CH-P), 108.34 (d, $J(C-P)$ = 5.4 Hz, CHβ furan), 110.67 (s, CHβ furan), 142.27 (d, $J(C-P)$ = 2 Hz, CHα furan), 150.71 (d, $^2J(C-P)$ = 8.2 Hz, Cα furan), 205.76 (d, $^2J(C-P)$ = 9.4 Hz, cis CO), 209.90 (d, $^2J(C-P)$ = 23 Hz, trans CO). Mass spectrum (^{98}Mo): m/z 432 (M^+, 39), 317 (100). Anal. Calcd for $C_{16}H_{15}MoO_6P$: C, 44.65; H, 3.49. Found: C, 44.49; H, 3.66.

2-(2-Thienyl)-1,3,4-trimethyl-2,5-dihydrophosphole 1-Oxide (10). To complex **2**[3] (5.34 g, 1×10^{-2} mol) in 20 mL of CH_2Cl_2 at 0 °C were slowly added first pyridinium tribromide (3.5 g, 95% purity, 1.1×10^{-2} mol) and then *N*-methylimidazole (4.4 mL, 5×10^{-2} mol). The reactions were monitored by ^{31}P NMR spectroscopy: δ ^{31}P +14 ppm after the addition of Br_3^- and +12 ppm after the addition of the base. The reaction mixture was hydrolyzed (2 h) and neutralized (HCl). After extraction, drying, and evaporation, the organic residue was chromatographed with ethyl acetate/methanol, 95/5, as the eluent. Yield: 1.15 g (50%) of a yellow oil. ^{31}P NMR (CH_2Cl_2): δ + 59.1 ppm. ^1H NMR ($CDCl_3$): δ 1.27 (d, $^2J(H-P)$ = 12.9 Hz, 3 H, Me-P), 1.74 (s, 3 H, Me-C), 1.87 (m, 3 H, Me-C), 2.62 (m, 2 H, CH_2-P), 4.22 (d, $^2J(H-P)$ = 19.3 Hz, 1 H, CH-P), 6.74–7.24 (m, 3 H, thiophene). ^{13}C NMR ($CDCl_3$): δ 13.01 (d, $^1J(C-P)$ = 67 Hz, Me-P), 14.85 (d, $^3J(C-P)$ = 9.6 Hz, Me-C), 17.04 (d, $^3J(C-P)$ = 11.9 Hz, Me-C), 37.93 (d, $^1J(C-P)$ = 64.3 Hz, CH_2-P), 53.22 (d, $^1J(C-P)$ = 65.8 Hz, CH-P), 124.48 (d, $J(C-P)$ = 3.6 Hz, CH thiophene), 125.41 (d, $J(C-P)$ = 6.2 Hz, CH thiophene), 127.59 (d, $J(C-P)$ = 2.2 Hz, CH thiophene), 129.98 (d, $^2J(C-P)$ = 7 Hz, Me-*C*), 131.24 (d, $^2J(C-P)$ = 12.1 Hz, Me-*C*), 139.58 (s, C thiophene). Mass spectrum: m/z 226 (M^+, 100).

1-Phenyl-2-(2-thienyl)-3,4-dimethyl-2,5-dihydrophosphole 1-Oxide (11). The same experimental procedure as for **10** was used. Starting with complex **7** (12 g, 2×10^{-2} mol), pyridinium tribromide (6.72 g), and *N*-methylimidazole (8 mL), 2.9 g (~50%) of a yellow oil was obtained after chromatography with ethyl acetate as the eluent. ^{31}P NMR (CH_2Cl_2): δ 51.7 ppm. ^1H NMR ($CDCl_3$): δ 1.73 (s, 3 H, Me), 1.90 (s, 3 H, Me), 2.67 (pseudo t, 1 H, CH_2), 3.00 (pseudo d, 1 H, CH_2), 4.34 (d, $^2J(C-P)$ = 19.7 Hz, 1 H, CH-P), 6.50, 6.64, and 6.86 (3 pseudo s, 3 × 1 H, CH thiophene), 7.17–7.46 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.71 (d, $^3J(C-P)$ = 9.5 Hz, Me), 15.90 (d, $^3J(C-P)$ = 12 Hz, Me), 35.57 (d, $^1J(C-P)$ = 65.4 Hz, CH_2-P), 52.97 (d, $^1J(C-P)$ = 66 Hz, CH-P), 123.12 (d, $J(C-P)$ = 2.2 Hz, CH thiophene), 124.43 (d, $J(C-P)$ = 6.2 Hz, CH thiophene), 125.77 (s, CH thiophene), 137.46 (d, $^2J(C-P)$ = 3.4 Hz, C thiophene). Mass spectrum: m/z 289 ($M^+ + H$, 100).

1-Phenyl-2-(*p*-methoxyphenyl)-3,4-dimethyl-2,5-dihydrophosphole 1-Sulfide (12). Complex **8** (5.32 g, 1×10^{-2} mol) and sulfur (2.5 g, $\sim 8 \times 10^{-2}$ mol) were refluxed in toluene (20 mL) for 2 h. After filtration and evaporation, the organic residue was chromatographed first with hexane to remove sulfur and then with toluene/ethyl acetate, 90/10, to get the product. Yield: 2.3 g (70%) of white crystals. ^{31}P NMR (CH_2Cl_2): δ 57.3 ppm. ^1H NMR ($CDCl_3$): δ 1.63 (s, 3 H, Me), 1.95 (s, 3 H, Me), 2.99 (m, 1 H, CH_2), 3.40 (m, 1 H, CH_2), 3.58 (s, 3 H, MeO), 4.30 (d, $^1J(H-P)$ = 16 Hz, 1 H, CH-P), 6.50 (*AB*, $^3J(H-H)$ = 8 Hz, 2 H, anisole), 6.62 (*AB*, 2 H, anisole), 7.15 (m, 3 H, Ph meta, para), 7.45 (m, 2 H, Ph ortho). ^{13}C NMR ($CDCl_3$): δ 14.43 (d, $^3J(C-P)$ = 9.6 Hz, Me), 16.53 (d, $^3J(C-P)$ = 12 Hz, Me), 42.13 (d, $^1J(C-P)$ = 52.4 Hz, CH_2-P), 54.69 (s, OMe), 64.45 (d, $^1J(C-P)$ = 49.1 Hz, CH-P), 157.94 (d, $^5J(C-P)$ = 2.6 Hz, *C*-OMe). Mass spectrum: m/z 328 (M^+, 100). Anal. Calcd for $C_{19}H_{21}OPS$: C, 69.57; H, 6.40. Found: C, 69.47; H, 6.39.

2-(2-Furyl)-1,3,4-trimethyl-2,5-dihydrophosphole 1-Sulfide [13(S)]. Complex **9** (4.3 g, 1×10^{-2} mol) and sulfur (2.6 g, ~8 × 10^{-2} mol) were refluxed in toluene for 3 h. The organic residue was chromatographed with hexane/ethyl acetate, 80/20, as the eluent. Yield: 1.7 (75%) of a yellow oil. ^{31}P NMR (CH_2Cl_2): δ + 55.5 ppm. ^1H NMR ($CDCl_3$): δ 1.47 (d, $^2J(H-P)$ = 13 Hz, 3 H, Me-P), 1.66 (s, 3 H, Me-C), 1.83 (s, 3 H, Me-C), 2.65–3.10 (m,

2 H, CH_2-P), 4.22 (d, ^2J(H-P) = 15.7 Hz, 1 H, CH-P), 6.21 (m, 1 H, Hβ furan), 6.36 (m, 1 H, Hβ furan), 7.40 (m, 1 H, Hα furan). ^{13}C NMR ($CDCl_3$): δ 14.71 (d, ^3J(C-P) = 9.2 Hz, Me-C), 16.88 (d, ^3J(C-P) = 11.3 Hz, Me-C), 18.12 (d, ^1J(C-P) = 50.6 Hz, Me-P), 43.79 (d, ^1J(C-P) = 51 Hz, CH_2-P), 57.07 (d, ^1J(C-P) = 51.2 Hz, CH-P), 108.54 (d, J(C-P) = 7.2 Hz, Cβ furan), 110.80 (d, J(C-P) = 2.3 Hz, Cβ furan), 128.75 (d, ^2J(C-P) = 11.8 Hz, Me-*C*), 129.59 (d, ^2J(C-P) = 6 Hz, Me-*C*), 142.52 (d, ^4J(C-P) = 2.9 Hz, CHα' furan), 149.14 (d, ^2J(C-P) = 8.5 Hz, Cα furan). Mass spectrum: m/z 227 (M^+ + H, 100), 226 (M^+, 100). Anal. Calcd for $C_{11}H_{15}OPS$: C, 58.41; H, 6.64. Found: C, 57.65; H, 6.60.

1-Phenyl-2-(2-thienyl)-3,4-dimethylphosphole (14). Phosphine oxide **11** (7 g, 2.4×10^{-2} mol) and phenylsilane (3 mL, 2.4×10^{-2} mol) were refluxed in dry degassed toluene (5 mL) for 3 h. The reaction was monitored by ^{31}P NMR: δ^{31}P (phosphine) −9.2 ppm. The toluene was evaporated and replaced by dry degassed dichloromethane (50 mL). The resulting solution was cooled with ice and pyridinium tribromide (8 g, 2.4×10^{-2} mol) was added portionwise. At the end of the addition, the reaction was monitored by ^{31}P NMR: δ^{31}P (bromophosphonium bromide) +67 ppm. The flask containing the solution was kept in the ice bath, and α-picoline (4.7 mL, 4.8×10^{-2} mol) was added dropwise to the reaction mixture. As soon as the addition was completed, the reaction was again monitored by ^{31}P NMR and the hydrolysis was performed with deoxygenated water. After the usual workup, the organic residue was chromatographed on deoxygenated silica gel with hexane/ether, 95/5, as the eluent. Yield: 4.5 g (70%) of a yellow oil which slowly crystallized. ^{31}P NMR (CH_2Cl_2): δ +6.6 ppm. ^{1}H NMR (C_6D_6): δ 1.54 (dd, ^4J(H-P) = 3.17 Hz, ^4J(H-H) = 1.46 Hz, 3 H, Me-C_4), 1.74 (d, ^4J(H-P) = 3.17 Hz, 3 H, Me-C_3), 6.03 (dm, 1 H, ^2J(H-P) = 38.6 Hz, = CH-P), 6.32–7.26 (m, 8 H, Ph + thiophene). ^{13}C NMR (C_6D_6: δ 15.10 (s, Me), 18.55 (s, Me). Mass spectrum: m/z 270 (M^+, 100). Anal. Calcd for $C_{16}H_{15}PS$: C, 71.11; H, 5.56. Found: C, 71.29; H, 5.69.

2-(2-Thienyl)-1,3,4-trimethylphosphole (15) and Its *P*-Sulfide 18. Same experimental procedure as for **14**. The reduction of phosphine oxide **10** (1.13 g, 5×10^{-3} mol) by phenylsilane (0.62 mL, 5×10^{-3} mol) was completed in 40 min. δ^{31}P (phosphine) −30 ppm. The bromination at phosphorus was carried out by pyridinium tribromide (1.68 g, 95% purity, 5×10^{-3} mol): δ^{31}P (bromophosphonium bromide) +79 ppm. The dehydrobromination was performed with α-picoline (0.97 mL, 1×10^{-2} mol). Heavy losses were observed during the chromatography due to the high sensitivity of **15** toward oxygen. The oxidation of **15** was easily monitored by ^{31}P NMR: the oxide is dimeric δ^{31}P +54.89 and +80.25 ppm, ^3J(P-P) 39 Hz. Yield of **15**: ca. 0.1 g (10%). ^{31}P NMR (CH_2Cl_2): δ −8.4 ppm. ^{1}H NMR (C_6D_6): δ 1.14 (d, ^2J(H-P) = 1.5 Hz, 3 H, Me-P), 1.86 (dd, ^4J(H-P) = 2.7 Hz, ^4J(H-H) = 1.5 Hz, 3 H, Me-C_4), 2.03 (d, ^4J(H-H) = 3 Hz, 3 H, Me-C_3), 6.26 (d broad, ^2J(H-P) = 39.5 Hz, =CH-P), 6.80–7.16 (m, 3 H, thiophene). ^{13}C NMR (C_6D_6): δ 8.72 (d, ^1J(C-P) = 19.2 Hz, Me-P), 14.90 (s, Me-C), 18.51 (s, Me-C), 149.79 (d, ^1J(C-P) = 3.5 Hz, C_2). Mass spectrum: m/z 208 (M^+, 100). The product was analyzed as its *P*-sulfide **18**. Anal. Calcd for $C_{11}H_{13}PS_2$: C, 55.0; H, 5.42. Found: C, 54.64; H, 5.32.

1-Phenyl-2-(*p*-methoxyphenyl)-3,4-dimethylphosphole (16). Phosphine sulfide **12** (3.28 g, 1×10^{-2} mol) and tributylphosphine (3.5 mL, 2×10^{-2} mol) were refluxed in toluene (5 mL) for 2.5 h. The reaction was monitored by ^{31}P NMR: δ^{31}P (dihydrophosphole) −9 ppm. The dihydrophosphole was quickly chromatographed on a well degassed silica gel column with hexane/ether, 95/5, as the eluent. It was obtained as a colorless oil (2.22 g, 0.75×10^{-2} mol) very sensitive toward oxygen. This oil was dissolved in dry oxygen-free dichloromethane (20 mL). The flask was cooled with a ice bath and pyridinium tribromide (2.52 g, 0.75×10^{-2} mol) was added portionwise: δ^{31}P (bromophosphonium bromide) +70 ppm. Then, α-picoline (1.5 mL, 1.5×10^{-2} mol) was added dropwise. After the usual workup, the organic residue was chromatographed with hexane/ether, 95/5, as the eluent. Yield: 1.54 g (70%) of a colorless oil. ^{31}P NMR (CH_2Cl_2): δ +4.8 ppm. ^{1}H NMR ($CDCl_3$): δ 2.10 (d, ^4J(H-P) = 2.8 Hz, 3 H, Me-C_3), 2.15 (dd, ^4J(H-P) = 3.3 Hz, ^4J(H-H) = 1.4 Hz, 3 H, Me-C_4), 3.72 (s, 3 H, OMe), 6.45 (d broad, ^2J(H-P) = 40 Hz, 1 H, =CH-P), 6.81 (AB, ^3J(H-H) = 8.7 Hz, 2 H, anisyl), 7.11–7.25 (m, 7 H, phenyl + B). ^{13}C NMR ($CDCl_3$): δ 14.48 (s, Me), 18.48 (s, Me), 55.00 (s, OMe), 140.85 (d, J(C-P) = 13.1 Hz), 146.07 (s, C_2?), 150.52 (d, J(C-P) = 7 Hz, C_3?), 158.03 (s, *C* OMe). Mass spectrum of the *P*-sulfide: m/z 326 (M^+, 100).

2-(2-Furyl)-1,3,4-trimethylphosphole 1-Sulfide (19). Phosphine sulfide **13** (2.26 g, 1×10^{-2} mol) was stirred with cyclohexene oxide (2.2 mL, 2.1×10^{-2} mol) and trifluoroacetic acid (1.6 mL, 2.1×10^{-2} mol) in dry CH_2Cl_2 at room temperature. After 5 min, the P=S → P=O conversion was complete according to ^{31}P NMR analysis: δ^{31}P +70 ppm (see ref 10 for the use of this technique). The reaction mixture was hydrolyzed and neutralized by a 10% solution of sodium carbonate. The crude phosphine oxide was used as such. Same experimental procedure as for **14**. The reduction of the phosphine oxide (2.1 g, 1×10^{-2} mol) by phenylsilane (1.24 mL, 1×10^{-2} mol) was completed in 45 min: δ^{31}P (dihydrophosphole) −29 ppm. Pyridinium tribromide (3.36 g, 1×10^{-2} mol) was used for the bromination: δ^{31}P (dibromophosphorane) + 79 ppm. α-Picoline (2 mL, 2×10^{-2} mol) and 0.32 g of sulfur were simultaneously added to the mixture for the conversion of the dibromophosphorane into the phosphole sulfide. After the usual workup, the organic residue was chromatographed with hexane/ethyl acetate, 70/30, as the eluent. Yield: 1.12 g (50%) of yellow crystals. ^{31}P NMR (CH_2Cl_2): δ +47.2 ppm. ^{1}H NMR ($CDCl_3$): δ 1.87 (d, ^2J(H-P) = 13.6 Hz, 3 H, Me-P), 2.10 (dd, ^4J(H-P) ~ ^4J(H-H) ~ 1.7 Hz, 3 H, Me-C_4), 2.31 (d, ^4J(H-P) 1.9 Hz, 3 H, Me-C_3), 6.08 (d, ^2J(H-P) = 32 Hz, 1 H, =CH-P), 6.50 (m, 1 H, Hβ furan), 6.92 (d, 1 H, Hβ furan), 7.53 (s, 1 H, Hα furan). ^{13}C NMR ($CDCl_3$): δ 14.76 (d, ^3J(C-P) = 13.4 Hz, Me-C), 17.86 (d, ^3J(C-P) = 17.5 Hz, Me-C), 19.50 (d, ^1J(C-P) = 52.6 Hz, Me-P), 111.09 (s, Cβ furan), 111.52 (s, Cβ furan), 121.47 (d, ^1J(C-P) = 82.7 Hz, =CH-P), 126.15 (d, ^1J(C-P) = 80.9 Hz, C_2-P), 141.16 (d, ^2J(C-P) = 22.08 Hz, Me-*C*), 142.70 (s, CHα' furan), 148.36 (d, ^2J(C-P) = 22.02 Hz, Me-*C*), 153.90 (d, ^2J(C-P) = 16.15 Hz, Cα furan). Mass spectrum: m/z 224 (M^+, 100). Anal. Calcd for $C_{11}H_{13}OPS$: C, 58.93; H, 5.80. Found: C, 59.15; H, 5.97.

[1-Phenyl-2-(2-thienyl)-3,4-dimethylphosphole]pentacarbonyltungsten (20). Hexacarbonyltungsten (3.9 g, 1.1×10^{-2} mol) was irradiated for 50 min in dry THF at room temperature (400-W medium-pressure mercury lamp). Phosphole **14** (2.7 g, 1×10^{-2} mol) was added to the solution. After 20 min of stirring, the solution was evaporated and the organic residue was chromatographed with hexane/ether, 95/5, as the eluent. Yield: 5.9 g (~100%) of pale yellow crystals. ^{31}P NMR (CH_2Cl_2): δ +22.5 ppm, $^1J(^{31}P-^{183}W)$ = 222 Hz. ^{1}H NMR ($CDCl_3$): δ 2.26 (s broad, 3 H, Me), 2.32 (s broad, 3 H, Me), 6.51 (d, ^2J(H-P) = 36.8 Hz, 1 H, =CH-P), 6.79 (m, 1 H, Hβ thiophene), 6.93 (m, 1 H, Hβ thiophene), 7.22 (m, 1 H, Hα thiophene), 7.4–7.6 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ 15.12 (d, ^3J(C-P) = 8.1 Hz, Me), 18.05 (d, ^3J(C-P) = 10.2 Hz, Me), 196.00 (d, ^2J(C-P) = 6 Hz, cis CO), 198.33 (d, ^2J(C-P) = 20.4 Hz, trans CO). Mass spectrum (^{184}W): m/z 594 (M^+, 18), 454 (M^+ − 5CO, 100). Anal. Calcd for $C_{21}H_{15}O_5PSW$: C, 42.57; H, 2.53. Found: C, 42.38; H, 2.27.

[1-Phenyl-2-(5-acetyl-2-thienyl)-3,4-dimethylphosphole]pentacarbonyltungsten (21). Acetyl chloride (freshly distilled) (0.16 mL, 2.2×10^{-3} mol) and $AlCl_3$ (0.3 g, 2.2×10^{-3} mol) were stirred for 20 min in CH_2Cl_2 (20 mL) at room temperature. Phosphole complex **20** (0.6 g, 1×10^{-3} mol) in CH_2Cl_2 solution was added to the mixture at room temperature. After 10 min, the solution was slowly poured into a saturated aqueous solution of NH_4Cl mixed with crushed ice. After extraction with CH_2Cl_2 and evaporation, the organic residue was chromatographed with hexane/ether, 90/10, as the eluent. Yield: 0.63 g (~100%) of yellow crystals. ^{31}P NMR (CH_2Cl_2): δ +22.5 ppm. ^{1}H NMR ($CDCl_3$): δ 2.29 (s broad, 3 H, Me), 2.39 (s broad, 3 H, Me), 2.48 (s, 3 H, C(O)Me, 6.60 (d, ^2J(H-P) = 37.7 Hz, 1 H, =CH-P), 6.78 (dd, ^3J(H-H) = 3.9 Hz, ^4J(H-P) = 1 Hz, 1 H, Hβ thiophene), 7.4–7.6 (m, 6 H, Ph + Hβ' thiophene). ^{13}C NMR ($CDCl_3$): δ 15.67 (d, ^3J(C-P) = 8 Hz, Me), 18.08 (d, ^3J(C-P) = 10 Hz, Me), 26.69 (s, C(O)*Me*), 190.42 (s, *C*(O)Me), 195.96 (d, ^2J(C-P) = 6.5 Hz, cis CO), 198.00 (d, ^2J(C-P) = 20.4 Hz, trans CO). Mass spectrum (^{184}W): m/z 635 (M^+ − H, 8.5), 496 (M^+ − 5CO, 100). Anal. Calcd for $C_{23}H_{17}O_6PSW$: C, 43.40; H, 2.67. Found: C, 43.46; H, 2.80.

[1-Phenyl-2-(5-formyl-2-thienyl)-3,4-dimethylphosphole]pentacarbonyltungsten (22). Phosphole complex **20** (0.56 g, 0.94×10^{-3} mol), *N*-methyl-*N*-phenylformamide (0.25 mL, 2×10^{-3} mol), and $POCl_3$ (0.2 mL, 2×10^{-3} mol) were refluxed in dichloromethane (20 mL). After 1.5 h, the reaction mixture was poured into a 10% aqueous solution of sodium carbonate

mixed with ice. The aqueous phase was extracted with dichloromethane, and the organic layer was washed with water until neutrality. After evaporation of the solvent, the organic residue was chromatographed with hexane/ether, 60/40, as the eluent. Yield: 0.31 g (ca. 50%) of a yellow solid, which was recrystallized in CH_2Cl_2/hexane. ^{31}P NMR (CH_2Cl_2): δ +24.0 ppm, $^1J(^{31}P\text{-}^{183}W)$ = 224.6 Hz. ^1H NMR ($CDCl_3$): δ 2.31 (s broad, 3 H, Me), 2.40 (s broad, 3 H, Me), 6.64 (d, ^2J(H-P) = 37.3 Hz, 1 H, =CH-P), 6.87 (d, ^3J(H-H) = 4 Hz, 1 H, Hβ thiophene), 7.43-7.58 (m, 5 H, Ph), 7.59 (d, ^3J(H-H) = 4 Hz, 1 H, Hβ' thiophene), 9.81 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ 15.53 (d, ^3J(C-P) = 8 Hz, Me), 17.92 (d, ^3J(C-P) = 10.5 Hz, Me), 182.58 (s, CHO), 195.66 (d, ^2J(C-P) = 6.5 Hz, cis CO), 197.72 (d, ^2J(C-P) = 20 Hz, trans CO). Mass spectrum (^{184}W): m/z 622 (M^+, 19), 481 (M^+ - 5CO - H, 100). Anal. Calcd for $C_{22}H_{15}O_6PSW$: C, 42.44; H, 2.41. Found: C, 42.17; H, 2.48.

A New Version of the Peterson Olefination Using Bis(trimethylsilyl)methyl Derivatives and Fluoride Ion as Catalyst

Claudio Palomo,* Jesus M. Aizpurua, Jesus M. García, Iñaki Ganboa, F. P. Cossio, Begoña Lecea, and Concepción López

Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072.20080, San Sebastián, Spain

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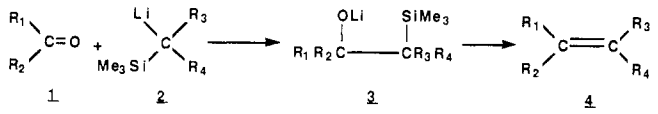
Reaction between a variety of bis(trimethylsilyl)methyl derivatives and carbonyl compounds under fluoride ion as catalyst is described. The reaction works especially well with nonenolizable carbonyl compounds to give the expected alkenes in high yields and, in some cases, with high stereoselectivity. Application of this methodology to an intramolecular alkenation providing a tricyclic benzocarbacephem ring system is also described.

The Peterson reaction[1] (eq 1) has proved to be one of the best methodologies for carbonyl olefination. Conceptually, it involves reaction between a carbonyl component **1** and an α-silyl carbanion **2**, followed by acidic or basic elimination of the resulting β-hydroxyalkylsilane **3**. This



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method is a powerful alternative to the Wittig olefination,[2] especially because the elimination step can be directed in either a syn or an anti manner[3] and, also, because a wider range of alkenes can be obtained from a wide variety of α-lithio silanes.[4] Recently, the use of fluoride ion as promoter of carbon nucleophiles from organosilicon compounds has become a field of considerable importance in organic synthesis.[5] Several groups have demonstrated that desilylation of organosilanes containing a C-SiR_3 bond by means of fluoride ion is an effective way for the transfer of carbanions to electrophilic centers.[6] However, very few examples have been described concerning the formation of α-silyl carbanions promoted by fluoride ion on organosilicon compounds involving two trialkylsilyl units in the same carbon atom.[7] Recently, we undertook a study on this subject, and found[8] that *N*-[bis(trimethylsilyl)-

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