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Preparations and Sulfurization Reactions of (2,4-Di-*t*-butyl-6-methoxyphenyl)phosphine and 1-(2,4-Di-*t*-butyl-6-methoxyphenyl)-2-(2,4,6-tri-*t*-butylphenyl)diphosphene

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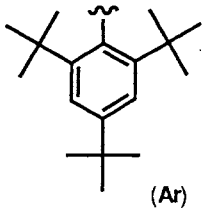
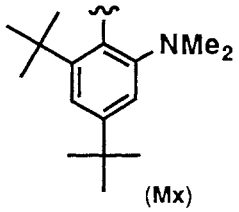
A phosphonous dichloride carrying 2,4-di-*t*-butyl-6-methoxyphenyl as a novel sterically protecting group was prepared and converted to an unsymmetrical diphosphene, which reacted with sulfur to give the corresponding diphosphene sulfide and thiadiphosphirane. The phosphonous dichloride was reduced to the corresponding primary phosphine, which was sulfurized to a dithioxophosphorane. The dithioxophosphorane reacted with benzophenone to give thiobenzophenone.

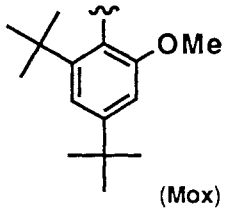
Low-coordinated phosphorus compounds such as diphosphenes, dithioxophosphoranes, and diselenoxophosphoranes are of interest because of their physicochemical properties.[1] However, they are usually unstable, unless kinetically stabilized by bulky substituents. Utilizing extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) as a sterically protecting auxiliary, we have been successful in the preparation and characterization of diphosphene ArP=PAr[2] and stable dithioxophosphorane $ArP(=S)_2$.[3] We have also utilized 2,4-di-*t*-butyl-6-(dimethylamino)phenyl group (abbreviated to Mx) as a new sterically protecting group and prepared extremely stable dithioxophosphorane $MxP(=S)_2$ and diselenoxophosphorane $MxP(=Se)_2$, as well as the first selenoxophosphine MxP=Se.[4] Apparently, Mx-substituted thioxo- and selenoxophosphoranes are more stable than the 2,4,6-tri-*t*-butylphenyl analogs, probably because of the contribution of thermodynamic stabilization caused by some interaction between the phosphorus atom and the dimethylamino group involving the lone pair electrons.

As a part of our continuing studies on sterically protected organophosphorus compounds in low coordination states, we report here the preparation and utilization of a new sterically protecting group: 2,4-di-*t*-butyl-6-methoxyphenyl (hereafter abbreviated to Mox: methoxy-*m*-xylene derivative), where the ortho dimethylamino group in the Mx is replaced by the methoxy group. This modulation may give us some insight into the role of the nitrogen of the Mx group and the oxygen of the Mox group.


(Ar)

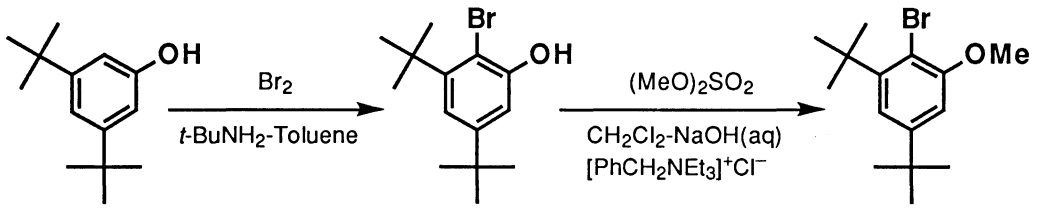


(Mx)



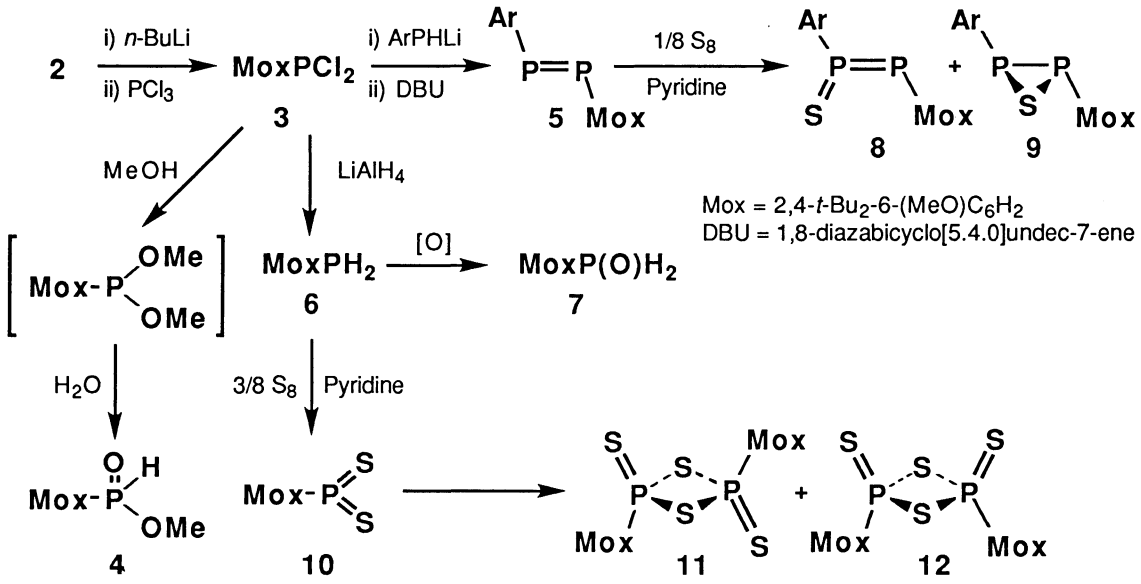
(Mox)

2-Bromo-3,5-di-*t*-butylphenol (**1**)[5] was prepared by the reaction of 3,5-di-*t*-butylphenol with Br_2 in the presence of *t*-$BuNH_2$.[6] The bromophenol **1** was then methylated by dimethyl sulfate to give 2-bromo-1,5-di-*t*-butyl-3-methoxybenzene (**2**).[7]



1 **2** (≡ MoxBr)

Treatment of **2** with butyllithium and successively with phosphorus trichloride gave the corresponding phosphonous dichloride **3**[7] in 79% yield. Quenching of **3** with methanol led to the formation of methyl 2,4-di-*t*-butyl-6-methoxyphenylphosphinate (**4**),[7] which was isolated in 85% yield after chromatography on silica gel.



Attempted preparation of a symmetrical diphosphene MoxP=PMox by coupling reaction of **3** with either magnesium or lithium naphthalenide in THF has been unsuccessful. The reaction of **3** with ArPHLi, however, followed by the dehydrochlorination reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave an unsymmetrical diphosphene **5** in 81% yield. The phosphonous dichloride **3** was reduced with lithium aluminum hydride to a primary phosphine **6** almost quantitatively. **5**: Deep orange oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.33 (18H, s, *o*-Bu^t), 1.38 (9H, s, Bu^t), 1.47 (9H, s, Bu^t), 1.55 (9H, s, Bu^t), 3.83 (3H, s, OMe), 6.89 (1H, s, Mox), 7.24 (1H, s, Mox), and 7.49 (2H, s, Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 502.8 and 448.5, AB, $^1J_{PP}$ = 562.0 Hz; MS (70 eV) *m/z* (rel intensity) 526 (M^+; 6), 277 (ArP^++1; 100), and 57 (*t*-Bu^+; 89); Found: *m/z* 526.3511. Calcd for $C_{33}H_{52}OP_2$: M, 526.3493. **6**: ^{1}H NMR (C_6D_6) δ = 1.25 (9H, s, Bu^t), 1.51 (9H, s, Bu^t), 3.34 (3H, s, OMe), 4.16 (2H, d, $^1J_{PH}$ = 207.5 Hz, PH_2), 6.65 (1H, bs, Mox), and 7.24 (1H, dd, $^4J_{HH}$ = 1.8 Hz, $^4J_{PH}$ = 3.0 Hz, Mox); ^{31}P NMR (C_6D_6) δ = −155.4 (t, $^1J_{PH}$ = 207.4 Hz); MS *m/z* 252 (M^+; 43) and 57 (*t*-Bu^+; 100); Found: *m/z* 252.1631. Calcd for $C_{15}H_{25}OP$: M, 252.1643. The phosphine **6** was partially oxidized with aerial oxygen to the corresponding phosphine oxide **7**.[7]

For the purpose of getting some insight into the stabilizing effect of Mx group on $MxP(=S)_2$,[4] sulfurization reaction of the Mox-substituted compounds **5** and **6** were studied. The diphosphene **5** reacted with elemental sulfur (1 equiv.) for 8 h in benzene at room temperature in the presence of pyridine to give a stable diphosphene sulfide **8** and thiadiphosphirane **9** in 35 and 12% isolated yields, respectively.[8] **8**: Yellow crystals, mp > 95 °C (decomp); ^{1}H NMR (600 MHz, C_6D_6) δ = 1.16 (9H, s, Bu^t), 1.35 (9H, s, Bu^t), 1.68 (9H, s, Bu^t), 1.72 (9H, s, Bu^t), 1.77 (9H, s, Bu^t), 3.35 (3H, s, OMe), 6.59 (1H, s), 7.24 (1H, d, $^4J_{PH}$ = 2.8 Hz), 7.67 (1H, s), and 7.72 (1H, s); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ = 56.3 (s, OMe), 124.3 (dd, $^1J_{PC}$ = 45.3 Hz and $^2J_{PC}$ = 14.6 Hz, *ipso*-Mox), 127.1 (dd, $^1J_{PC}$ = 63.8 Hz and $^2J_{PC}$ = 15.2 Hz, *ipso*-Ar); ^{31}P{^{1}H} NMR (C_6D_6) δ = 224.9 and 245.3, AB, $^1J_{PP}$ = 613.7 Hz; UV (hexane) 250 (log ε 4.21), 288 (sh, 3.95), and 373 (3.78); IR (KBr) 758, 725, and 644 cm^{-1}; MS *m/z* 558 (M$^+$; 1), 501 (M$^+$–Bu^t; 39), 313 (M$^+$–Ar; 100), and 57 (*t*-Bu$^+$; 80); Found: *m/z* 558.3189. Calcd for $C_{33}H_{52}OP_2S$: M, 558.3214. **9**: Colorless crystals, mp 119.5–120.5 °C; ^{1}H NMR (200 MHz, C_6D_6) δ = 1.14 (9H, s, Bu^t), 1.15 (9H, s, Bu^t), 1.56 (9H, s, Bu^t), 1.79 (18H, d, $^5J_{PH}$ = 0.9 Hz, *o*-Bu^t), 3.34 (3H, s, OMe), 6.53 (1H, d, $^4J_{HH}$ = 1.6 Hz, Mox), 7.15 (1H, dd, $^4J_{HH}$ = 1.6 Hz and $^4J_{PH}$ = 3.3 Hz, Mox), and 7.31 (2H, d, $^4J_{PH}$ = 1.43 Hz, Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 54.7 (s, OMe); ^{31}P{^{1}H} NMR (C_6D_6) δ = –81.8 and –67.6, AB, $^1J_{PP}$ = 247.0 Hz; IR (KBr) 924, 874, 847, 746 and 658 cm^{-1}; MS *m/z* 558 (M$^+$; 1), 501(M$^+$–Bu^t; 39), 313 (M$^+$–Ar; 100), 298 (M$^+$–Ar–Me; 6), and 57 (*t*-Bu$^+$; 50); Found: *m/z* 558.3224. Calcd for $C_{33}H_{52}OP_2S$: M, 558.3214.

The reaction of phosphine **6** with 3 equiv. of elemental sulfur at room temperature in benzene for 3 h in the presence of pyridine led to the formation of **10**: ^{31}P NMR (C_6D_6) δ = 277.6; MS *m/z* 314 (M$^+$; 10), 299 (M$^+$–Me; 4), 282 (M$^+$–S; 17), 256 (M$^+$–1–Bu^t; 99), 64 (S_2^+; 100), and 57 (*t*-Bu$^+$; 42); Found: *m/z* 314.0918. Calcd for $C_{15}H_{23}OPS_2$: M, 314.0928. In solution under an inert atmosphere, the compound **10** was stable for several days. In marked contrast to the extremely stable $MxP(=S)_2$, the Mox-derivative **10** dimerized to **11**[7] and **12**[7] in 18 and 15% isolated yields, respectively, even during the work-up process of evaporation of the solvent. Apparently, the stabilizing interaction of the methoxy group to the phosphorus atom in the Mox derivatives is much smaller than that of dimethylamino group in the Mx derivatives.

This moderately stable Mox-$P(=S)_2$ **10** allowed us to investigate its thiation ability. In the thiation reaction of carbonyl compounds with Lawesson's reagent [LR; 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide], species of the $RP(=S)_2$ type has been postulated as a reactive intermediate.[9] However, the mechanism of LR has been unclear because of the difficulty of the detection of unstable monomeric dithioxophosphoranes. Much stabilized analogs such as $MxP(=S)_2$ or $ArP(=S)_2$ did not react with ketones such as benzophenone. However, the reaction of **10** with benzophenone (in refluxing benzene, 24 h) led to the formation of thiobenzophenone in 12% isolated yield. Our results might support the proposed mechanism of LR.

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4) M. Yoshifuji, M. Hirano, and K. Toyota, *Tetrahedron Lett.*, **34**, 1043 (1993).

5) **1**: Colorless crystals, mp 114.5–115.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.30 (9H, s), 1.51 (9H, s), 5.92 (1H, s), 6.98 (1H, d, ^4J = 2.4 Hz), and 7.04 (1H, d, ^4J = 2.4 Hz); IR (KBr) 3700-3200, 1020, 968, and 858 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 286 (M^++2; 22), 284 (M^+; 22), 271 (M^+–Me+2; 49), 269 (M^+–Me; 48), and 57 (Bu^{t+}; 100); Found: C, 58.83; H, 7.36; Br, 27.56%. Calcd for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42; Br, 28.01%.

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7) **2**: Colorless crystals, mp 47.5–48.0 °C; ^{1}H NMR ($CDCl_3$) δ = 1.33 (9H, s), 1.54 (9H, s), 3.90 (3H, s), 6.83 (1H, d, ^4J = 2.2 Hz), and 7.12 (1H, d, ^4J = 2.2 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 56.6 (OMe); IR (KBr) 1070, 1024, and 849 cm^{-1}; MS *m/z* 300 (M^++2; 46), 298 (M^+; 47), and 57 (*t*-Bu^+; 100); Found: C, 60.17; H, 7.53; Br, 26.29%. Calcd for $C_{15}H_{23}BrO$: C, 60.21; H, 7.75; Br, 26.70%. **3**: Colorless crystals, mp 97.5–99.5 °C ; ^{1}H NMR ($CDCl_3$) δ = 1.34 (9H, s), 1.55 (9H, d, $^5J_{PH}$ = 0.7 Hz), 3.97 (3H, s), 6.91 (1H, d, $^4J_{HH}$ = 1.7 Hz), and 7.08 (1H, dd, $^4J_{HH}$ = 1.7 Hz and $^4J_{PH}$ = 6.1 Hz); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 159.3; IR (KBr) 1363, 1053, and 484 cm^{-1}; MS *m/z* 320 (M^+; 78) and 285 (M^+–Me; 100); Found: *m/z* 320.0858. Calcd for $C_{15}H_{23}Cl_2OP$: M, 320.0864. **4**: Colorless crystals, mp 76.5–77.5 °C; ^{1}H NMR ($CDCl_3$) δ = 1.28 (9H, s), 1.48 (9H, s), 3.82 (3H, d, $^3J_{PH}$ = 12.6 Hz), 3.89 (3H, s), 6.84 (1H, dd, $^4J_{PH}$ = 4.3 Hz and $^4J_{HH}$ = 1.5 Hz), 7.13 (1H, dd, $^4J_{PH}$ = 5.5 Hz and $^4J_{HH}$ = 1.5 Hz), and 8.11 (1H, d, $^1J_{PH}$ = 584.3 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 53.0 (d, $^2J_{PC}$ = 6.4 Hz, POMe), and 56.5 (s, Mox-OMe); ^{31}P NMR ($CDCl_3$) δ = 28.3 (d, $^1J_{PH}$ = 584.0 Hz); IR (KBr) 2441, 2384, 1240, 1221, and 1219 cm^{-1}; MS *m/z* 298 (M^+; 59) and 283 (M^+–Me; 100); Found: *m/z* 298.1714. Calcd for $C_{16}H_{27}O_3P$: M, 298.1698. **7**: Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.33 (9H, s), 1.53 (9H, s), 3.96 (3H, s), 6.89 (1H, dd, $^4J_{PH}$ = 4.2 Hz and $^4J_{HH}$ = 1.5 Hz), 7.19 (1H, dd, $^4J_{PH}$ = 5.0 Hz and $^4J_{HH}$ = 1.5 Hz), and 7.92 (2H, d, $^1J_{PH}$ = 490.1 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 56.6 (s, OMe); ^{31}P NMR ($CDCl_3$) δ = –12.0 (t, $^1J_{PH}$ = 490.0 Hz); MS *m/z* 268 (M^+; 21) and 57 (*t*-Bu^+; 100); Found: *m/z* 268.1572. Calcd for $C_{15}H_{25}O_2P$: M, 268.1592. **11**: Colorless crystals, mp 217.5–218.5 °C ; ^{1}H NMR ($CDCl_3$) δ = 1.34 (18H, s), 1.65 (18H, s), 4.02 (6H, s), 6.86 (2H, dd, $^4J_{HH}$ = 1.8 Hz and $^4J_{PH}$ = 5.9 Hz), and 7.27 (2H, dd, $^4J_{HH}$ = 1.8 Hz and $^4J_{PH}$ = 7.4 Hz); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 56.9 (s, OMe); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 30.5; IR (KBr) 920, 677, 598, and 482 cm^{-1}; MS *m/z* 628 (M^+; 18), 314 ($MoxPS_2^+$; 90), 281 ($MoxPS^+$–1; 100), and 57 (*t*-Bu^+; 15); MW ($CHCl_3$) 623; Found: *m/z* 628.1855. Calcd for $C_{30}H_{46}O_2P_2S_4$: M, 628.1855. **12**: Colorless crystals, mp > 121 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 1.26 (18H, s), 1.46 (18H, s), 3.98 (6H, s), 6.76 (2H, dd, $^4J_{HH}$ = 1.6 Hz and $^4J_{PH}$ = 5.8 Hz), and 7.11 (2H, dd, $^4J_{HH}$ = 1.6 Hz and $^4J_{PH}$ = 7.2 Hz); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 56.8 (s, OMe); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 29.9; IR (KBr) 912, 737, 729, 700, 681, 596, 488, and 472 cm^{-1}; FAB-MS *m/z* 629 (M^++1), 314 ($MoxPS_2^+$), and 57 (*t*-Bu^+).

8) In the dark, the reaction gave only **8** in 44% yield, indicating that **9** might be formed by room light; M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, **1983**, 862.

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