Tetrahedron Letters, Vol. 34, No. 6, pp. 1043-4046, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Stable Dithioxophosphorane, Diselenoxophosphorane, and Selenoxophosphine Bearing 2,4-Di-*t*-butyl-6-(dimethylamino)phenyl Group as a New Sterically Protecting Auxiliary

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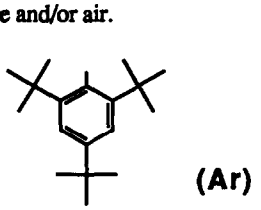
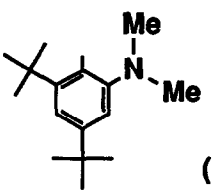
Key Words: Steric Protection; Diphosphene; Diselenoxophosphorane; Selenoxophosphine

Abstract: *2,4-Di-t-butyl-6-(dimethylamino)phenylphosphonous dichloride was prepared from 2-bromo-3,5-di-t-butyl-N,N-dimethylaniline. The dichloride was then converted to the corresponding diphosphene. The reaction of the diphosphene with sulfur or selenium in triethylamine afforded 2,4-di-t-butyl-6-(dimethylamino)-phenyldithioxophosphorane or diselenoxophosphorane, respectively, as a very stable compound and the diselenoxo-phosphorane was deselenated with hexamethylphosphorous triamide to give selenoxophosphine.*

Compounds with low coordinated heavier main group elements such as phosphorus can be kinetically stabilized by bulky substituents (steric protection).[1] 2,4,6-Tri-*t*-butylphenyl group (hereafter abbreviated to Ar) is one of the typical bulky protecting groups[2] and by utilizing this substituent we and others have successfully prepared various types of low coordinated tervalent phosphorus compounds such as diphosphenes, phosphaalkenes, phosphacumulenes, and phosphaalkynes. Low coordinated hypervalent phosphorus compounds of chalcogenophosphine type ($\sigma^2\lambda^3$ coordination state) or monomeric metaphosphate type ($\sigma^3\lambda^5$ coordination state) are of current interest.[1] The latter species are particularly important with respect to ATP hydrolysis. Using the Ar group, some $\sigma^3\lambda^5$ coordinated phosphorus species such as dithioxo-phosphorane[3] and diselenoxophosphorane[4] have been isolated as thermally stable compounds, although they are sensitive to moisture and/or air.



(Ar)

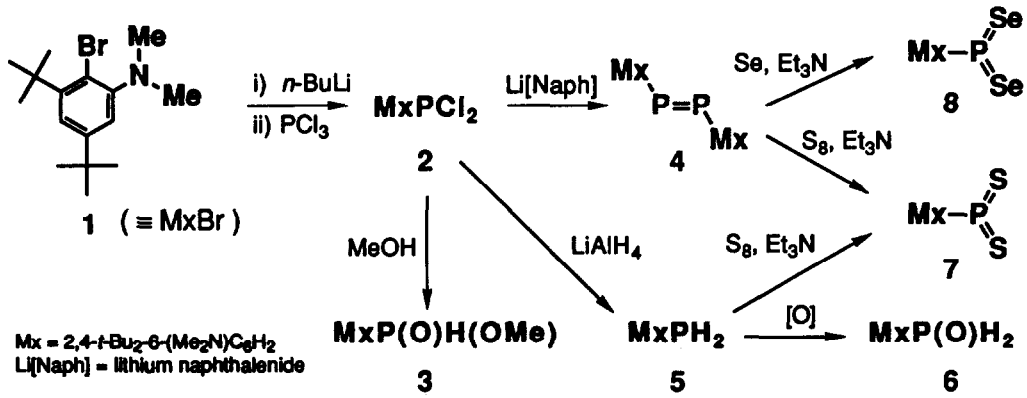


(Mx)

During the course of our studies on unusual organophosphorus compounds, we have examined 2,4-di-*t*-butyl-6-methylphenyl,[5] 2,6-di-*t*-butylphenyl,[6] and 2,4,6-tri-*t*-pentylphenyl[7] groups as protecting auxiliary to evaluate the stabilization effect of substituents at the *ortho* positions of the groups. We now report the utilization of 2,4-di-*t*-butyl-6-(dimethylamino)phenyl group (hereafter abbreviated to Mx from "octamethylxylidine") as a new protecting group, where one of the *ortho* *t*-butyl groups in the Ar is replaced by

dimethylamino group.[8] The Mx group is expected to be bulky enough to contribute to kinetic stabilization. In addition, the *o*-dimethylamino group may show an electronic effect on stabilization because the lone pair electrons may affect the delocalized π-system through bond or space. Consequently, the substituent Mx can be considered a 'hybrid' protecting group of both kinetic and thermodynamic effect.

2-Bromo-3,5-di-*t*-butyl-*N*,*N*-dimethylaniline (**1**)[9] was prepared by methylation of 2-bromo-3,5-di-*t*-butylaniline.[10] Treatment of **1** with butyllithium and phosphorus trichloride gave 2,4-di-*t*-butyl-6-(dimethylamino)phenylphosphonous dichloride (**2**): $^{31}P\{^1H\}$ NMR (81 MHz, THF + C_6D_6) δ = 154.9. Because of the instability, **2** was used for subsequent reactions without purification. Quenching of **2** with methanol gave methyl 2,4-di-*t*-butyl-6-(dimethylamino)phenylphosphinate (**3**) in 48% yield (based on **1**) after silica-gel column chromatography.[11]



1,2-Bis[2,4-di-*t*-butyl-6-(dimethylamino)phenyl]diphosphene (**4**) was prepared by addition of a THF solution of lithium naphthalenide to a THF solution of **2** at –78 °C. **4**: $^{31}P\{^1H\}$ NMR (THF + C_6D_6) δ = 428.2; MS(70 eV) *m/z* (rel intensity) 526 (M^+; 6), 294 (MxP_2; 7), 264 (MxP+1; 100), and 233 (Mx+1; 34); Found: *m/z* 526.3606. Calcd for $C_{32}H_{52}N_2P_2$: M, 526.3606. An attempted purification of **4** by flash column chromatography (SiO_2) was not successful due to the decomposition during the chromatographic treatment.

The phosphonous dichloride **2** was reduced to the primary phosphine **5** by lithium aluminum hydride. The phosphine **5** was partially oxidized with aerial oxygen to the corresponding phosphine oxide **6** during the isolation process using silica-gel column chromatography.[12]

We have already reported the reaction of bis(2,4,6-tri-*t*-butylphenyl)diphosphene with elemental sulfur to give diphosphene monosulfide which was rearranged to the thiadiphosphirane by heat or light.[13] However, the reaction of **4** (prepared from 0.33 mmol of **1**) with elemental sulfur (0.78 mg-atom) in triethylamine (10 ml) at room temperature for 1 day gave [2,4-di-*t*-butyl-6-(dimethylamino)phenyl]dithioxophosphorane **7** (24% yield based on **1**). **7**: Colorless crystals; mp 267–268 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.34 (9H, s, *t*-Bu), 1.55 (9H, s, *t*-Bu), 3.25 (6H, d, $^5J_{PH}$ = 7.3 Hz, NMe), 7.12 (1H, dd, $^4J_{PH}$ = 2.6 Hz and $^4J_{HH}$ = 1.5 Hz, arom.), and 7.52 (1H, dd, $^4J_{PH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 170.6; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 31.2 (s, C<u>Me</u>$_3$), 35.8 (s, <u>C</u>Me$_3$), 36.2 (s, <u>C</u>Me$_3$), 47.0 (s, NMe), 111.3 (d, $^3J_{PC}$ = 11.3 Hz, *m*-arom.), 126.4 (d, $^3J_{PC}$ = 13.5 Hz, *m*-arom.), 139.5 (d, $^1J_{PC}$ = 95.5 Hz, *ipso*-arom.), 147.6 (s, arom.), 151.5 (d, $^2J_{PC}$ = 3.2 Hz, arom.), and 157.7 (d, $^2J_{PC}$ = 2.8 Hz, arom.); UV (CH_2Cl_2) 259 nm (log ε 3.9); IR (KBr) 2956, 1479, 1456, 725, and 653 cm^{-1}; mol wt (benzene) 345; MS (70

eV) *m/z* (rel intensity) 327 (M^+; 64) and 294 (MxPS–1; 100); Found: *m/z* 327.1255. Calcd for $C_{16}H_{26}NPS_2$: M, 327.1244. The compound **7** was alternatively prepared by the reaction of the phosphine **5** with elemental sulfur (20% yield based on **1**), similarly to the case of the sulfurization of 2,4,6-tri-*t*-butylphenylphosphine.[3c]

Similarly, the diselenoxophosphorane **8** was obtained (35% yield based on **1**) by the reaction of **4** with selenium in triethylamine at room temperature for 1 day. **8**: Pale yellow crystals; mp 275–277 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 1.33 (9H, s, *t*-Bu), 1.58 (9H, s, *t*-Bu), 3.20 (6H, d, $^5J_{PH}$ = 7.4 Hz, NMe), 7.07 (1H, dd, $^4J_{PH}$ = 2.7 Hz and $^4J_{HH}$ = 1.4 Hz, arom.), and 7.53 (1H, dd, $^4J_{PH}$ = 8.1 Hz and $^4J_{HH}$ = 1.4 Hz, arom.); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 149.6 (accompanied with satellite d, $^1J_{PSe}$ = 819.6 Hz); ^{77}Se{^{1}H} NMR (38 MHz, $CDCl_3$) δ = 399.6 (d, $^1J_{PSe}$ = 818.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 31.2 (s, $C\underline{Me}_3$), 31.5 (s, $C\underline{Me}_3$), 35.8 (s, $\underline{C}Me_3$), 36.6 (s, $\underline{C}Me_3$), 46.6 (s, NMe), 112.1 (d, $^3J_{PC}$ = 9.7 Hz, *m*-arom.), 126.6 (d, $^3J_{PC}$ = 12.6 Hz, *m*-arom.), 139.5 (d, $^1J_{PC}$ = 66.0 Hz, *ipso*-arom.), 148.2 (d, $^4J_{PC}$ = 3.8 Hz, arom.), 151.6 (d, $^2J_{PC}$ = 2.7 Hz, arom.), and 157.7 (d, $^2J_{PC}$ = 2.7 Hz, arom.); UV (CH_2Cl_2) 248 (log ε 4.2) and 286 nm (3.9); IR (KBr) 1454, 980, 582, and 478 cm^{-1}; mol wt (benzene) 466; MS *m/z* (rel intensity) 423 (M^+; 37), 263 (M^+–2Se; 100), and 232 (M^+–PSe_2; 5); Found: *m/z* 423.0134. Calcd for $C_{16}H_{26}NPSe_2$: M, 423.0133. The ^{31}P NMR spectrum of **8** shows satellite signals around the phosphorus signal (d, relative intensity: 13.8%) due to ^{77}Se (natural abundance 7.58%), which indicates the existence of two equivalent selenium nuclei on one phosphorus atom supporting the diselenoxophosphorane structure. The relatively large coupling constants $^5J_{PH}$ observed for compounds **7** and **8** indicate that there is some interaction between the phosphorus atom and the dimethylamino group involving lone pair, while the protons of *o*-*t*-butyl group did not couple with the phosphorus atom. Either compound **5** or **6** did not give any evidence of such interaction between the phosphorus and the dimethylamino protons.

Attempted desulfurization of **7** with either triphenylphosphine or hexamethylphosphorous triamide (HMPT) was not successful, in contrast to the reported results on the desulfurization reaction of 2,4,6-tri-*t*-butylphenyldithioxophosphorane with triphenylphosphine leading to the corresponding trithiatriphosphorinane.[14] Apparently, **7** is more stable than its 2,4,6-tri-*t*-butylphenyl derivative probably because of the thermodynamic stabilization caused by *o*-dimethylamino group. On the other hand, the diselenoxophosphorane **8** was successfully deselenated with excess amount of HMPT to give the diphosphene **4**. Furthermore, the treatment of **8** with 1 mol equiv. of HMPT led to the formation of selenoxophosphine **9** of $\sigma^2\lambda^3$ type. **9**: ^{1}H NMR (THF-d_8) δ = 1.32 (9H, s, *t*-Bu), 1.38 (9H, s, *t*-Bu), 2.79 (3H, s, NMe), 3.09 (3H, d, $^5J_{PH}$ = 5.5 Hz, NMe), 7.11 (1H, pseudo t, $^4J_{PH}$ = $^4J_{HH}$ = 1.6 Hz, arom.), and 7.45 (1H, pseudo t, $^4J_{PH}$ = $^4J_{HH}$ = 1.9 Hz, arom.); ^{31}P{^{1}H} NMR (THF-d_8) δ = 399.0 (accompanied with satellite d, $^1J_{PSe}$ = 708.7 Hz, rel intensity 7.9%); ^{77}Se{^{1}H} NMR (THF-d_8) δ = 521.3 (d, $^1J_{PSe}$ = 708.0 Hz). The compound **9** was metastable and disproportionation reaction occurred in THF at room temperature for 1 day to give **4** and **8**. This reaction might proceed *via* an oligomer of **9**. Some minor signals were observed in the region of cyclopolyphosphines (δ_P –50 to –100) by ^{31}P NMR study during the reaction, although the structures have not been characterized. Attempts to trap **9** with dienes or as a metal complex are now in progress.

$$\mathbf{8} \xrightarrow{P(NMe_2)_3} \underset{\mathbf{9}}{MxP{=}Se} \longrightarrow \mathbf{4} + \mathbf{8}$$

This work was supported in part by the Grants-in-Aid for Scientific Research (Nos. 02403008 and 03214101) from the Ministry of Education, Science and Culture, Japanese Government and the Asahi Glass

Research Fund from the Asahi Glass Foundation. They also thank Shin-Etsu Chemical Co., Ltd. for donating organosilicon compounds and Tosoh Akzo Co., Ltd. for organolithium reagents.

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11. **3**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.31 (9H, s, *t*-Bu), 1.52 (9H, s, *t*-Bu), 2.72 (6H, s, NMe), 3.83 (3H, d, $^3J_{PH}$ = 12.7 Hz, OMe), 7.19 (1H, dd, $^4J_{PH}$ = 4.0 Hz and $^4J_{HH}$ = 1.8 Hz, arom.), 7.39 (1H, dd, $^4J_{PH}$ = 5.6 Hz and $^4J_{HH}$ = 1.8 Hz, arom.), and 7.96 (1H, d, $^1J_{PH}$ = 591.1 Hz, PH); ^{31}P NMR (81 MHz, $CDCl_3$) δ = 29.2 (d, $^1J_{PH}$ = 591.1 Hz); MS (25 eV) *m/z* (rel intensity) 311 (M^+; 17) and 233 (Mx+1; 100).
12. **5**: ^{1}H NMR ($CDCl_3$) δ = 1.32 (9H, s, *t*-Bu), 1.50 (9H, s, *t*-Bu), 2.68 (6H, s, NMe), 4.14 (2H, d, $^1J_{PH}$ = 213.9 Hz), 7.12 (1H, dd, $^4J_{PH}$ = 2.1 Hz and $^4J_{HH}$ = 2.1 Hz, arom.), and 7.32 (1H, dd, $^4J_{PH}$ = 2.1 Hz and $^4J_{HH}$ = 2.1 Hz, arom.); ^{31}P NMR ($CDCl_3$) δ = –141.6 (t, $^1J_{PH}$ = 213.7 Hz). **6**: ^{1}H NMR ($CDCl_3$) δ = 1.34 (9H, s, *t*-Bu), 1.58 (9H, s, *t*-Bu), 2.80 (6H, s, NMe), 7.26 (1H, dd, $^4J_{PH}$ = 3.3 Hz and $^4J_{HH}$ = 1.6 Hz, arom.), 7.43 (1H, dd, $^4J_{PH}$ = 5.5 Hz and $^4J_{HH}$ = 1.6 Hz, arom.), and 7.82 (2H, d, $^1J_{PH}$ = 485.1 Hz, PH); ^{31}P NMR ($CDCl_3$) δ = –13.7 (t, $^1J_{PH}$ = 484.9 Hz).
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(Received in Japan 21 September 1992)