Pergamon

Tetrahedron Letters, Vol. 35, No. 23, pp. 3971-3974, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0717-C

Preparation and X-Ray Structure of [2,4-Di-*t*-butyl-6-(*N*,*N*-dimethylaminomethyl)phenyl]dithioxophosphorane Stabilized by Intramolecular Coordination

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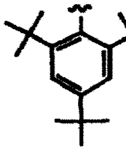
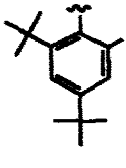
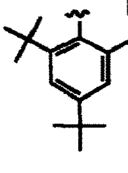
Abstract: [2,4-Di-*t*-butyl-6-(*N*,*N*-dimethylaminomethyl)phenyl]dithioxophosphorane was prepared by the reaction of the corresponding phosphine and elemental sulfur. The structure of the dithioxophosphorane was analyzed by X-ray crystallography, which indicated a strong participation of the nitrogen lone pair in the stabilization of the dithioxophosphoryl group.

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 and powerful 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.[1] We are now engaged in developing new protecting groups which are expected to contribute to both kinetic and thermodynamic stabilization. Very recently, we have reported the utilization of 2,4-di-*t*-butyl-6-(dimethylamino)phenyl group (abbreviated to Mx; Mx stands for octa<u>m</u>ethyl<u>x</u>ylidine derivative) as a new protecting group,[3] where one of the *o*-*t*-butyl groups in the Ar is replaced by an electron donating dimethylamino group. Utilizing this substituent, we have prepared MxP=S[4] and MxP=Se[3] for the first time as well as MxP(=S)$_2$ and MxP(=Se)$_2$ as stable compounds. Since then, we have been interested in the role of the nitrogen lone pair of the Mx group and involved in modifying the Mx group with respect to the kind of element as well as the position of the hetero atom.


(Ar)

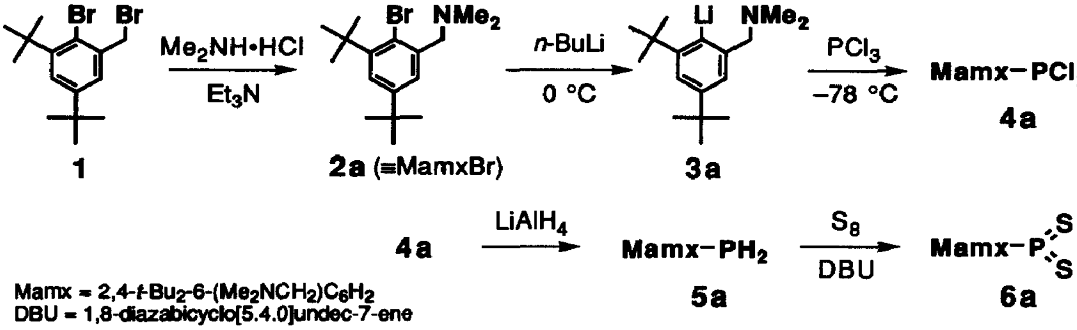


(Mx)



(Mamx)

Here, we report the utilization of 2,4-di-*t*-butyl-6-(*N*,*N*-dimethylaminomethyl)phenyl group (abbreviated to Mamx; Mamx stands for <u>m</u>ethyl<u>a</u>mino<u>m</u>ethyl-*m*-<u>x</u>ylene derivative) as a novel protecting group carrying both bulky *t*-butyl group and lone-pair containing dimethylaminomethyl group at the *o*-positions. Although the role of the dimethylamino group in the Mx group has not been well analyzed, the dimethylamino group in the Mamx group is expected to directly coordinate in an intramolecular fashion.[5]



2-Bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene (**1**)[6] was allowed to react with dimethylamine in dimethylformamide to give 2-bromo-1,5-di-*t*-butyl-3-(*N*,*N*-dimethylaminomethyl)benzene (**2a**) in 95% yield.[7] The bromobenzene **2a** was lithiated with butyllithium in Et_2O at 0 °C and the resulting solution containing **3a**[8] was added to an ethereal solution of PCl_3 at –78 °C. Reduction of the resulting phosphonous dichloride **4a** with $LiAlH_4$ afforded the primary phosphine **5a** [δ_P ($CDCl_3$) = –143.6 (t, $^1J_{PH}$ = 203.6 Hz)]. The phosphine **5a** was then allowed to react with elemental sulfur (3 equiv. as S) in benzene at room temperature in the presence of 0.25 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 2 h to give the corresponding dithioxophosphorane **6a** after column chromatography (12% yield based on **2a**). **6a**: Colorless silky needles, mp 236.0 – 237.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.30 (9H, s, Bu^t), 1.73 (9H, s, Bu^t), 3.09 (6H, d, J_{PH} = 7.6 Hz, NMe_2), 4.47 (2H, d, J_{PH} = 5.0 Hz, NCH_2), 7.00 (1H, dd, J_{PH} = 2.6 Hz and J_{HH} = 1.8 Hz, *m*-Mamx), and 7.54 (1H, dd, J_{PH} = 7.3 Hz and J_{HH} = 1.8 Hz, *m*'-Mamx); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ = 149.6; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 45.3 (d, J_{PC} = 3.1 Hz, NMe_2) and 62.3 (d, J_{PC} = 8.7 Hz, $\underline{C}H_2NMe_2$); UV (CH_2Cl_2) 254 (log ε 3.83), 284 (sh, 3.50), and 302 nm (sh, 3.08); IR (KBr) 713 and 634 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 341 (M^+; 18) and 308 (M^+–S–H; 100); MW (C_6H_6) 341; Found: *m/z* 341.1409. Calcd for $C_{17}H_{28}NPS_2$: M, 341.1401.

Table 1 shows ^{31}P NMR data of the dithioxophosphorane **6a** and some related compounds. Remarkable high-field shift was observed for **6a** compared to **6d** or ArP(=S)$_2$ **6e**. This fact indicates the strong interaction between the phosphorus atom and the nitrogen lone pair in **6a** and it was confirmed by the X-ray crystal structure analysis.[12] Figure 1 shows an ORTEP[13] drawing of **6a** in the crystal. It should be noted that the unit cell contains one solvent molecule (benzene) per **6a** entity, but the benzene was omitted for clarity in Fig. 1. The nitrogen lone pair of **6a** is directed toward the phosphorus atom and the distance between the nitrogen and the phosphorus (1.921(8) Å) is much shorter than the sum of the van der Waals radii, 3.4 Å, and is rather comparable to the P-N bond length for sodium hydrogenphosphoramidate (1.77(2) Å).[14] The dithioxophosphoryl group is distorted from planarity, thus the phosphorus atom is placed 0.34 Å above the plane (S1-S2-C1) in marked contrast to **6e**.[11b] This plane (S1-S2-C1) makes an angle of 72.5° with the benzene ring (C1–C6). Although the phosphorus atom is almost on the plane of the benzene ring (deviation of P1 from the plane is within 0.02 Å), the phosphorus atom is distorted toward the nitrogen atom making the angle P1-C1-C6 of 109.7(8)°. The atoms (P1, C1, C6, and C15) are coplanar within 0.01 Å and the nitrogen atom N1 is 0.70 Å above the plane, making the five-membered ring in an envelope type.

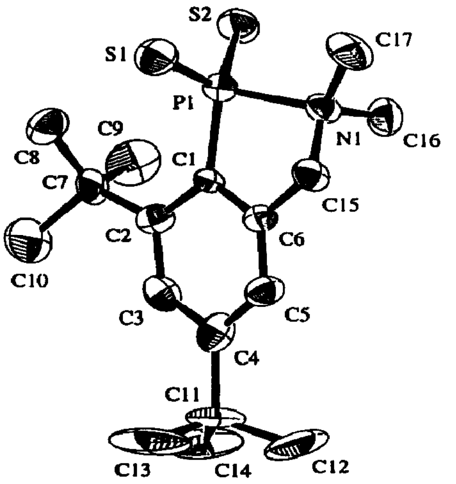
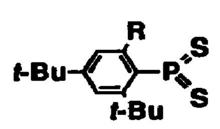


Figure 1. Structure of **6a** in the crystal (ellipsoids drawn at 50% probability level). Hydrogen atoms and the incorporated benzene are ommited for clarity. Some important bond lengths (Å) and angles (°): P1-S1, 1.944(4); P1-S2, 1.936(4); P1-C1, 1.820(9); P1-N1, 1.921(8); S1-P1-S2, 122.2(2); S1-P1-C1, 109.8(3); S2-P1-C1, 118.7(3); S1-P1-N1, 105.5(3); S2-P1-N1, 105.4(3); N1-P1-C1, 88.2(4); P1-C1-C2, 132.0(8); P1-C1-C6, 109.7(8).

Table 1. ^{31}P NMR of Some Dithioxophosphoranes

Compound	R	δ_P in $CDCl_3$
	**6a**: CH_2NMe_2	149.6
	6b: NMe_2[a]	170.6
	6c: OMe[b]	277.6[e]
	6d: Me[c]	285.2[f]
	6e: *t*-Bu[d]	298.2

a) Data taken from Ref. 3. b) Data from Ref. 9.
c) Data from Ref. 10. d) Data from Ref. 11a.
e) Measured in C_6D_6. f) Measured in toluene.

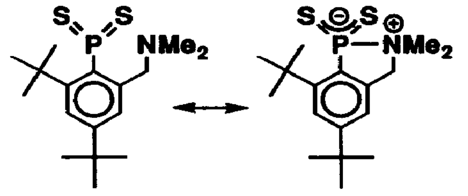


Figure 2. Resonance structure of **6a**.

The phosphorus-sulfur bond lengths for **6a** (1.944(4) Å for P1-S1 and 1.936(4) Å for P1-S2) are close to the P=S bond length for **6e** (1.90 Å) or that for Ph(*t*-Bu)P(=S)-S-S-P(=S)(*t*-Bu)Ph (**7**) (1.938(2) Å)[15] and are significantly shorter than phosphorus-sulfur single bond for **7** (2.153(1) Å). Thus, the structure is well represented by the contribution of the resonance structure as shown in Figure 2.

The resemblance of the ^{31}P NMR chemical shifts between $MxP(=S)_2$ **6b** and $MamxP(=S)_2$ **6a** may suggest that the major stabilizing factor in the Mx derivative **6b** is also due to through-space interaction such as intramolecular coordination. The bulky *t*-butyl group may secondarily afford kinetic stability, thus making the Mamx group, as well as the Mx group, useful for stabilization of the very reactive species with positively charged phosphorus.

Acknowledgment: This work was supported in part by the Grants-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japanese Government (Nos. 03233105 and 02403008) and the Research Fund from the Asahi Glass Foundation. The authors also thank Tosoh Akzo Co., Ltd., for donation of organolithium reagents.

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7. **2a**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 1.32$ (9H, s, Bu^t), 1.55 (9H, s, Bu^t), 2.31 (6H, s, NMe_2), 3.54 (2H, s, NCH_2), 7.29 (1H, d, $J = 2.6$ Hz, arom.), and 7.40 (1H, d, $J = 2.6$ Hz, arom.); MS (70 eV) *m/z* (rel intensity) 327 (M^++2; 50), 325 (M^+; 50), and 203 (M^+–NMe_2–Br+1; 100); Found: *m/z* 325.1369. Calcd for $C_{17}H_{28}BrN$: M, 325.1405.
8. When **3a** was quenched with methanol, 1,3-di-*t*-butyl-5-(*N,N*-dimethylaminomethyl)benzene was obtained: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 1.33$ (18H, s, Bu^t), 2.24 (6H, s, NMe), 3.42 (2H, s, CH_2), 7.13 (2H, d, $^4J = 1.7$ Hz, arom.), and 7.32 (1H, t, $^4J = 1.8$ Hz, arom.); MS (70 eV) *m/z* (rel intensity) 247 (M^+; 45), 133 (M^+–$2Bu^t$; 60), and 57 (*t*-Bu^+; 100); Found: *m/z* 247.2277. Calcd for $C_{17}H_{29}N$: M, 247.2300.
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12. Crystal data of **6a**: Recrystallized from benzene. $C_{17}H_{28}NPS_2 \cdot C_6H_6$, $M_r = 419.62$. Monoclinic, space group $P2_1/a$, $a = 12.156(2)$, $b = 12.840(6)$, $c = 15.901(2)$ Å; $\beta = 103.25(1)$; $V = 2416(1)$ Å^3, $Z = 4$, $\rho = 1.154$ gcm^{-3}, $\mu = 2.94$ cm^{-1}; 4467 independent reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer (MoKα radiation, graphite monochrometer). Of these, 1859 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELX86.[16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at the calculated positions, except for those on the *p*-*t*-butyl group and those on the benzene solvent molecule. $R = 0.073$, $R_w = 0.076$. Further details of the crystal structure investigation are available on request from Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, (UK), on quoting the full journal citation.
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(*Received in Japan* 7 *December* 1993; *accepted* 3 *March* 1994)