CHEMISTRY LETTERS, pp. 1931-1934, 1994.

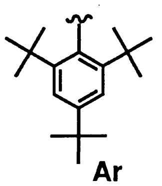
Preparation and Structure of Phenyldithioxophosphoranes Carrying *t*-Butyl and Dimethylaminomethyl or Dimethylaminoethyl Groups at the ortho-Positions

Masaaki YOSHIFUJI,* Kazunori KAMIJO, and Kozo TOYOTA
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980-77

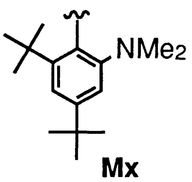
Dithioxophosphoranes and thioxophosphines carrying 2,4-di-*t*-butyl-6-(aminoalkyl)-phenyl groups were prepared and characterized. The intramolecular coordination of the nitrogen lone pair to the phosphorus atom was indicated by NMR and IR spectroscopy and was confirmed by X-ray crystallography.

Kinetic stabilization using bulky protecting groups is a useful method for investigation of low coordinated phosphorus compounds. Utilizing the extremely bulky 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Ar group) as a sterically protecting auxiliary, we and others have successfully prepared various types of multiply bonded phosphorus compounds such as diphosphenes1) and dithioxophosphorane.2) However, thioxophosphines are too reactive to be isolated even if being sterically protected with the Ar group.2c,3)

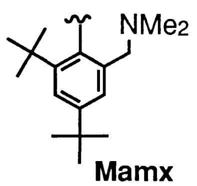
On the other hand, thermodynamic stabilization is an alternative method of stabilization of thioxophosphines. Recently, we have developed some novel stabilizing groups, such as 2,4-di-*t*-butyl-6-(dimethylamino)phenyl (Mx group)4) and 2,4-di-*t*-butyl-6-(dimethylaminomethyl)phenyl (Mamx group),5) having electron donating groups in their moieties. Using these substituents, dithioxophosphoranes as well as selenoxo- and thioxophosphines were prepared as stable compounds. In these compounds, the phosphorus-sulfur bonds are stabilized by both steric protection of the *o*-*t*-butyl group and thermodynamic stabilization caused by intramolecular coordination of the amino group of the substituents at ortho position. Now we developed novel stabilizing groups, 2,4-di-*t*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl (**I**) and 2,4-di-*t*-butyl-6-[1-(dimethylamino)-1-methylethyl]phenyl (**II**), which are expected to have more protecting and coordination ability than Mx or Mamx by formation of 6- or 5-membered ring.



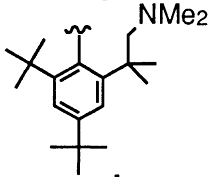
Ar



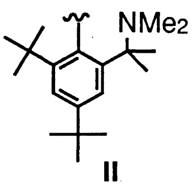
Mx



Mamx

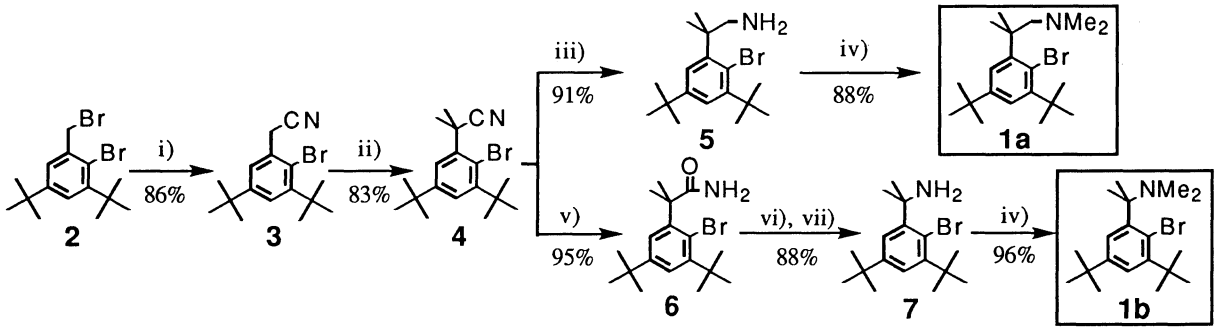


I



II

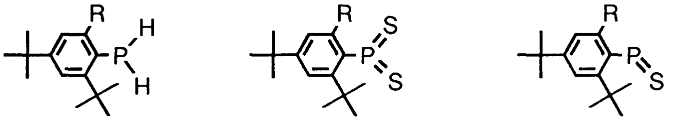
Sterically hindered bromobenzenes **1a**,**b**6) were prepared from 2-bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene (**2**)7) as shown in Scheme 1 via **3**, **4**, and **5** (57% overall yield of **1a**) or via **3**, **4**, **6**, and **7** (57% overall yield of **1b**) by the analogous method reported previously.8) The bromobenzene **1a** (368 mg; 1.08 mmol) was lithiated with butyllithium (1.5 equiv) under argon in ether (20 mL) at 0 °C and the resulting solution was added to an ethereal (20 mL) solution of PCl_3·(1.5 equiv), then the product was treated with lithium



i) KCN, 18-crown-6 / CH_3CN, H_2O; ii) CH_3I, NaOH, 18-crown-6 / DMSO, H_2O; iii) $LiAlH_4$ / Et_2O; iv) HCHO (aq), $NaBH_3CN$, AcOH / CH_3CN; v) H_2SO_4, AcOH, H_2O; vi) NaOMe, Br_2 / MeOH; vii) KOH, 18-crown-6 / DMSO, H_2O.

Scheme 1.

aluminum hydride (2.0 equiv) to give the corresponding phosphine **8a**. The phosphine **8a** thus obtained was allowed to react with S_8 (5.4 mmol as S) in benzene (10 mL) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.3 equiv) at room temperature for 10 h to give the corresponding dithioxophosphorane **9a** (13% yield based on **1a**). Very similarly, **9b** was prepared from **1b** (3% yield based on **1b**). Formation of thioxophosphines **10a,b** was observed by ^{31}P NMR and MS spectroscopy by the successive reaction of **1a,b** with butyllithium (1.6 equiv), PCl_3 (1.6 equiv), and hexamethyldisilathiane (0.5 equiv) as shown in Scheme 2.



8a-f **9a-f** **10a-f**

a: R=$CMe_2CH_2NMe_2$
b: R=CMe_2NMe_2
c: R=CH_2NMe_2
d: R=NMe_2
e: R=Me
f: R=*t*-Bu

$$\mathbf{10a,b} \xleftarrow{\text{i), ii), v)}} \mathbf{1a,b} \xrightarrow{\text{i), ii), iii)}} \mathbf{8a,b} \xrightarrow{\text{iv)}} \mathbf{9a,b}$$

i) *n*-BuLi / Et_2O; ii) PCl_3 / Et_2O; iii) $LiAlH_4$ / Et_2O; iv) S_8, DBU / C_6H_6; v) $(Me_3Si)_2S$, NEt_3 / Et_2O.

Scheme 2.

^{31}P NMR chemical shifts of the compounds **8a,b**, **9a,b**, **10a,b** and other related compounds are listed in Table 1. As for the phosphines **8a-f**, the effect of the amino group on the chemical shift are not apparent.[9)] On the contrary, interaction of nitrogen to phosphorus in the dithioxophosphoranes **9a-d** is clearly shown by ^{31}P NMR spectroscopy. The signals due to the dithioxophosphoranes **9a-d** appear at higher field by ca. 150 ppm than that of **9e,f**. This up-field shift is ascribable to the coordination of the nitrogen lone pair to the phosphorus atom in **9a-d**. In the case of **9a**, such internal coordination is performed by forming 6-membered ring, while 5- or 4-membered ring is formed in the case of **9b,c** or **9d**, respectively. Thus, the degree of observed up-field shift corresponds to the size of coordination ring. The largest up-field shift in **9a** indicates that 6-membered ring is highly efficient for the coordination. Efficiency of coordination is also indicated by IR spectroscopy, thus the absorption due to phosphorus-sulfur double bond shifts to lower wavenumber as the ring increases in size.

The six-membered ring coordination in **9a** was established by X-ray crystallographic analysis.[10)] Figure 1 depicts a molecular structure drawing of **9a** where *p-t*-butyl group is disordered and one with the higher occupancy factor is shown for clarity. The P=S bonds for **9a** (1.956(4), 1.946(4) Å) are longer than those for **9f** (1.90 Å)[2a)] and slightly longer than those for **9c** (1.944(4), 1.936(4) Å).[5)] This elongated bond length indicates that the multiplicity of P=S is decreased by the coordination. The P-N distance for **9a** (1.918(9) Å) is almost the same as that for **9c** (1.921(8) Å) and the most striking difference between **9a** and **9c** is the bond angles C1-P1-N1: 99.1(5)° for **9a** and 88.2(4)° for **9c**.

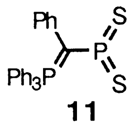
Table 1. $^{31}P\{^1H\}$ NMR and IR Data of **8**, **9**, and **10**

	8	**9**		**10**	
	δ_P a)	δ_P a)	ν (P=S) / cm^{-1}	δ_P b)	Ref.
a	−127.4	135.7	696 632	209.7	This work
b	−134.5	150.5	700 634	281.4	This work
c	−143.6	149.6	713 634	282.7	5
d	−141.6	170.6	725 653	388.5	4a,b
e	−143.0	285.2	—	—	11a,b
f	−129.9	298.2	792 660	—	11c,2c

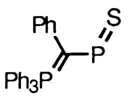
a) Measured in $CDCl_3$ except for **9e** (in toluene); the reported value of **8e**: −149.9 (in C_6D_6).[11a] b) Measured in C_6D_6; the reported value of **10d**: 382.0 (in THF-d_8).[4a]

The ^{31}P NMR signals of thioxophosphines **10a-d** show a similar tendency observed in the case of dithioxophosphoranes **9a-d** and the degree of up-field shift due to the difference in the ring size is larger than that of the **9a-d**, thus **10a,b** resonate at δ_P= 209.7 and 281.4, higher than that for **10d** about 180 or 100 ppm, respectively. This fact also indicates that the coordination becomes more effective by the increased ring size. Although thioxophosphines **10a,b** did not decompose in $CDCl_3$ solution for one day, attempted isolation was not successful because of decomposition in the air.

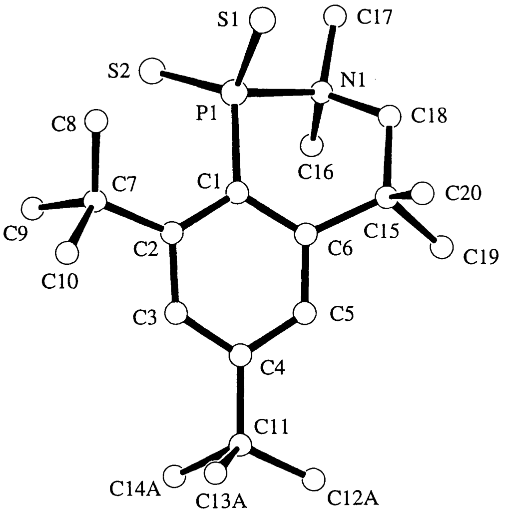
The thermodynamically stabilized compounds **11** (δ_P= 243)[12a] and **12** (δ_P= 495.9)[12b] was reported by Schmidpeter et al. to resonate at lower field than **9a-d** and **10a-d**, respectively. This fact indicates the existence of the large electronic perturbation in **10a-d**.

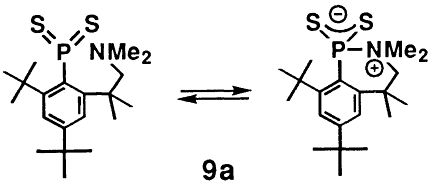


11



12





9a

Fig. 1. Molecular structure of **9a**. Some important bond lengths (Å) and bond angles(°): P1-S1, 1.956(4); P1-S2, 1.946(4); P1-C1, 1.83(1); P1-N1, 1.918(9); S1-P1-S2, 120.6(2); S1-P1-C1, 114.1(3); S2-P1-C1, 113.7(4); S1-P1-N1, 103.1(3); S2-P1-N1, 102.1(3); N1-P1-C1, 99.1(5); P1-C1-C2, 122.5(8); P1-C1-C6, 119.3(9); P1-N1-C18, 107.7(6); C1-C6-C15, 124(1); N1-C18-C15, 116.4(9); C6-C15-C18, 116.9(9).

In summary, preparations of thioxophosphines **10a,b** and dithioxophosphoranes **9a,b** were successful. ^{31}P NMR spectra and IR spectra indicated that ring size plays an important role in coordination structures. The new protecting groups **I**, **II** might be useful for stabilizing unstable molecules containing polarizable bonds.

References

1) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); **104**, 6167 (1982).

2) a) R. Appel, F. Knoch, and H. Kunze, *Angew. Chem., Int. Ed. Engl.*, **22**, 1004 (1983); b) J. Navech, J. P. Majoral, and R. Kraemer, *Tetrahedron Lett.*, **24**, 5885 (1983); c) M. Yoshifuji, K. Toyota, K. Ando, and N. Inamoto, *Chem. Lett.*, **1984**, 317.

3) B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, **1982**, 691.

4) a) M. Yoshifuji, M. Hirano, and K. Toyota, *Tetrahedron Lett.*, **34**, 1043 (1993); b) M. Yoshifuji, S. Sangu, M. Hirano, and K. Toyota, *Chem. Lett.*, **1993**, 1715.

5) M. Yoshifuji, K. Kamijo, and K. Toyota, *Tetrahedron Lett.*, **35**, 3971 (1994).

6) Selected spectroscopic data: **1a**: Colorless oil, ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 1.60$ (6H, s, $C\underline{Me_2}CH_2$), 3.08 (6H, s, NMe_2), and 2.17 (2H, s, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 28.6$ ($C\underline{Me_2}CH_2$), 47.6 (NMe_2), and 67.1 (CH_2); MS (70 eV, EI) *m/z* 366 (M^+–H). **1b**: Colorless crystals, mp 72.5–75.0 °C; ^{1}H NMR $\delta = 1.54$ (6H, s, $C\underline{Me_2}NMe_2$) and 2.15 (6H, s, NMe_2); ^{13}C NMR $\delta = 22.8$ ($C\underline{Me_2}NMe_2$) and 38.2 (NMe_2); MS *m/z* 353 (M^+). **3**: Colorless crystals, mp 79.0–80.0 °C; ^{1}H NMR $\delta = 3.90$ (2H, s, CH_2CN); ^{13}C NMR $\delta = 37.5$ ($\underline{C}H_2CN$); IR 2248 cm^{-1} ($C\equiv N$); MS *m/z* 307 (M^+). **4**: Colorless crystals, mp 157.5–159.0 °C; ^{1}H NMR $\delta = 1.93$ (6H, s, CMe_2CN); ^{13}C NMR $\delta = 28.9$ ($C\underline{Me_2}CN$); IR 2227 cm^{-1} ($C\equiv N$) ; MS *m/z* 335 (M^+). **5**: Colorless crystals, mp 176.0–178.0 °C; ^{1}H NMR $\delta = 1.11$ (2H, br. s, NH_2), 1.41 (6H, s, $C\underline{Me_2}CH_2$), and 3.29 (2H, s, CH_2); ^{13}C NMR $\delta = 27.8$ ($C\underline{Me_2}CH_2$) and 51.3 (CH_2NH_2); IR 3392 (N-H) and 3303 (N-H) cm^{-1}. **6**: Colorless crystals, mp 179.0–181.5 °C; ^{1}H NMR $\delta = 1.70$ (6H, s, $CMe_2C{=}O$) and 5.26 (2H, br. s, NH_2); ^{13}C NMR $\delta = 50.5$ ($\underline{C}Me_2C{=}O$); IR 3294 (br. N-H), 3153 (br. N-H), and 1691 (C=O) cm^{-1}. **7**: Colorless crystals, mp 174.5–176.0 °C; ^{1}H NMR $\delta = 1.73$ (6H, s, $C\underline{Me_2}NH_2$) and 2.33 (2H, br. s, NH_2); ^{13}C NMR $\delta = 31.7$ ($C\underline{Me_2}N$) and 55.5 ($\underline{C}Me_2N$); MS *m/z* 325 (M^+). **9a**: Colorless crystals, mp 278.0–280.0 °C; ^{1}H NMR $\delta = 1.59$ (6H, s, $C\underline{Me_2}CH_2$), 3.05 (6H, d, $J_{PH} = 7.7$ Hz, NMe_2), and 4.00 (2H, br. s, $C\underline{H_2}NMe_2$); ^{13}C NMR $\delta = 45.4$ (s, NMe_2) and 66.7 (s, CH_2); Found: *m/z* 383.1883. Calcd for $C_{20}H_{34}NPS_2$: M, 383.1870. **9b**: Colorless crystals, mp 264.0–265.0 °C; ^{1}H NMR $\delta = 1.97$ (6H, s, $C\underline{Me_2}NMe_2$) and 3.01 (6H, d, $J_{PH} = 8.4$ Hz, NMe_2); ^{13}C NMR $\delta = 42.4$ (d, $J_{PC} = 2.51$ Hz, NMe_2); Found: *m/z* 369.1693. Calcd for $C_{19}H_{32}NPS_2$: M, 369.1714. **10a** (not isolated): MS *m/z* (rel intensity) 351 (M^+; 4), 304 (M^+–Me–S; 32), and 58 ($CH_2NMe_2^+$; 100). **10b** (not isolated): MS *m/z* 337 (M^+; 54), 290 (M^+–Me–S; 95), and 57 (*t*-Bu$^+$; 100).

7) M. Yoshifuji, K. Kamijo, and K. Toyota, *Bull. Chem. Soc. Jpn.*, **66**, 3440 (1993).

8) K. R. Kopecky and M.-Y. Yeung, *Can. J. Chem.*, **66**, 374 (1988); M. Yoshifuji, K. Shimura, and K. Toyota, *Bull. Chem. Soc. Jpn.*, **67**, 1980 (1994).

9) Studies on the relationship between the structure and the chemical shift about **8** are in progress from the view point of both theoretical calculation and systematic modification of the substituent at ortho position.

10) Crystal data of **9a**: Recrystallized from $CHCl_3$. $C_{20}H_{34}NPS_2$, $M_r = 383.59$. Monoclinic, space group $P2_1/a$, $a = 12.356(6)$, $b = 10.07(1)$, $c = 18.31(1)$ Å; $\beta = 104.39(5)°$; $V = 2206(2)$ Å^3, $Z = 4$, $\rho = 1.155$ gcm^{-3}, $\mu = 3.16$ cm^{-1}; 4137 independent reflections with $2\theta \leq 50.1°$ were recorded on a four-circle diffractometer (MoKα radiation, graphite monochrometer). Of these, 1557 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86. *p-t*-Butyl was disordered and they were solved into two positions of *t*-butyl groups from the difference maps, and their occupancy factor were refined to be 0.67 and 0.33. Hydrogen atoms were included at calculated position except for the *p-t*-butyl. All hydrogen atoms and the disordered carbon atoms were refined isotropically. $R = 0.076$, $R_w = 0.080$. Further details of the crystal structure investigation are available on request from Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).

11) a) M. Baudler and J. Simon, *Chem. Ber.*, **121**, 281 (1988); b) A. S. Ionkin, V. M. Nekhoroshkov, and Yu. Ya. Efremov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1991**, 1654; *Chem. Abstr.*, **115**, 208108s (1991); c) M. Yoshifuji, K. Toyota, K. Shibayama, and N. Inamoto, *Chem. Lett.*, **1983**, 1653.

12) a) A. Schmidpeter, G. Jochem, K. Karaghiosoff, and C. Robl, *Angew. Chem., Int. Ed. Engl.*, **31**, 1350 (1992); b) G. Jochem, H. Nöth, and A. Schmidpeter, *Angew. Chem., Int. Ed. Engl.*, **32**, 1089 (1993).

(Received July 7, 1994)