Formation and Reactions of Stabilized [2,4-Di-*t*-butyl-6-(methylthiomethyl)phenyl]thioxophosphine

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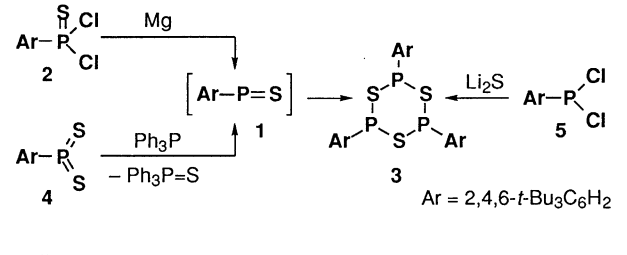
A stabilized thioxophosphine bearing the 2,4-di-*t*-butyl-6-(methylthiomethyl)phenyl group was generated either by reaction of the corresponding phosphonous dichloride with bis(trimethylsilyl) sulfide or by desulfurization reaction of the corresponding dithioxophosphorane using tris(dimethylamino)phosphine. The thioxophosphine, thus generated was trimerized to trithiatriphosphinane.

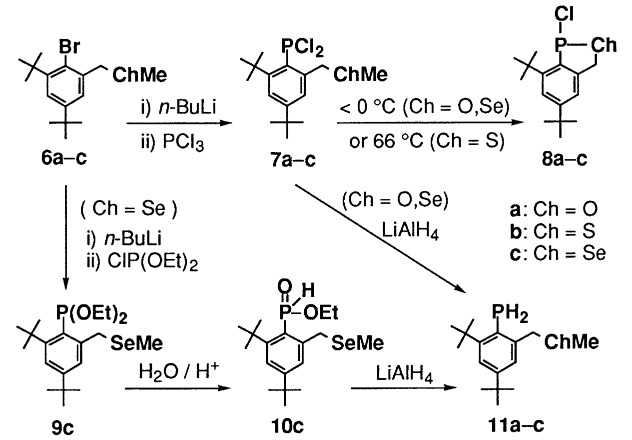
Reactive phosphorus species such as phosphinidenes,[1] oxophosphines,[2] and thioxophosphines[3] have attracted much interest for many years. The 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) is one of the typical and powerful sterically protecting groups, and by utilizing this substituent we and others have successfully prepared various types of phosphorus compounds of unusual structures such as diphosphenes,[4] phosphacumulenes,[5] and dithioxophosphorane.[6] Attempts were made to generate the Ar-substituted thioxophosphine **1** in the reaction of the corresponding phosphonothioic dichloride **2** with magnesium to result in formation of trithiatriphosphinane **3** [^{31}P NMR: δ_P ($CDCl_3$) = 91.0] and some other compounds such as the corresponding diphosphene and thiadiphosphirane.[6a] The generation of thioxophosphine **1** was also attempted by Navech et al. in the desulfurization reaction of the Ar-substituted dithioxophosphorane **4** with triphenylphosphine to result in the formation of **3**.[7] An alternative preparation of **3** by the reaction of phosphonous dichloride **5** with lithium disulfide was also reported in the literature.[8] However, the existence of **1** in these reactions has been unclear, because **1** has not been detected during these reactions as an intermediate.



In the course of our elaborate development on new stabilizing groups, we have examined various stabilizing groups having electron donating parts within the molecules.[9] Using these substituents, we have investigated preparation and properties of several dithioxophosphoranes and thioxophosphines, which are thermodynamically stabilized by intramolecular coordination. A stabilized thioxophosphine[10] bearing the 2,4-di-*t*-butyl-6-(dimethylamino)phenyl group has been generated,[9f] however, attempted isolation failed. Thus, information about the properties of the intramolecularly base-coordinated thioxophosphines has been limited. We now report here the utilization of the 2,4-di-*t*-butyl-6-(methylchalcogenomethyl)phenyl skeleton for investigation of stabilized thioxophosphines.

2-Bromo-1,5-di-*t*-butyl-3-(methylthiomethyl)benzene (**6b**) and its methylselenomethyl analogue **6c** were prepared by a method similar to that for 2-bromo-1,5-di-*t*-butyl-3-(methoxymethyl)benzene **6a**.[9c] Thus, reaction of 2-bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene with lithium methylselenide in THF at room temperature afforded **6c** in 93% yield. The methylthiomethyl derivative **6b** was prepared by a slightly modified method: A mixture of 2-bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene, sodium thiomethoxide (1.2 equiv.), hexadecyltributylphosphonium bromide (0.1 equiv.), benzene, and water, was stirred at ambient temperature for several hours to give **6b** in 98% yield.

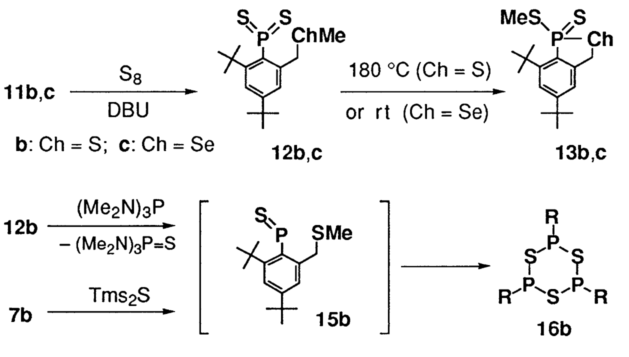
Lithiation of **6b** with butyllithium followed by the reaction with PCl_3 gave the corresponding phosphonous dichloride **7b** [δ_P (THF-C_6D_6) = 162]. Heating of **7b** in THF under reflux for 3 h led to an intramolecular cyclization product **8b** [δ_P = 151]. This cyclization reaction of **7b** in THF also proceeded but slowly at room temperature (ca. 6 days). Contrary to this, cyclization reaction of **7c** [δ_P = 162] to **8c** [δ_P = 156] proceeded below 0 °C. It should be noted that an analogous cyclization reaction of **7a** to **8a** occurred when a THF solution of **7a** was stirred at room temperature for 10 h.[9c] The relatively slow cyclization of **7b** may indicate that interaction between the phosphorus and sulfur atoms in **7b** is weaker than that between the phosphorus and oxygen (or selenium) atoms in **7a** (**7c**).



In order to avoid the intramolecular cyclization, the phosphorus moiety was alternatively introduced as follows. The reaction of **6c** with butyllithium (at ca. –100 °C) and diethyl phosphorochloridite in the presence of triethylamine gave **9c**. Then **9c** was converted to **10c** [colorless oil, δ_P ($CDCl_3$) = 28.5, $^1J_{PH}$ = 565 Hz] by hydrolysis (40% yield based on **6c**). Reduction of **7a**,**b**, and **10c** with $LiAlH_4$ in THF at 0 °C formed the corresponding phosphines **11a–c**, respectively.

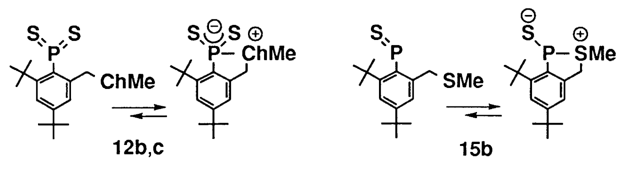
Attempted reactions of phosphine **11a** [δ_P ($CDCl_3$) = –148.6, $^1J_{PH}$ = 205.5 Hz], prepared *in situ*, with elemental sulfur in benzene in the presence of DBU at ambient temperature resulted in formation of a complex mixture of products. However, when phosphine **11b** [δ_P ($CDCl_3$) = –147.3, $^1J_{PH}$ = 205.5 Hz] was allowed to react with elemental sulfur under similar conditions, a stabilized dithioxophosphorane **12b** was obtained in 40% yield based on **6b**. **12b**: Colorless solid, mp 171–173 °C (decomp.); δ_P ($CDCl_3$) = 161.8; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ = 1.31 (9H, s, *p*-*t*-Bu), 1.74 (9H, s, *o*-*t*-Bu), 2.56 (3H, d, J_{PH} = 4.9 Hz, SMe), 4.50 (2H, br. s, benzyl), 7.01 (1H, m, arom.), and 7.50 (1H, m, arom.); IR (KBr) 703 and 619 cm^{-1}; MS *m*/*z* 344 (M^+).

When **11c** [δ_P ($CDCl_3$) = –147.6, $^1J_{PH}$ = 205.4 Hz] was allowed to react with elemental sulfur in benzene in the presence of DBU (0.1 equiv.) at room temperature for 1 day, compound **13c** (δ_P = 108) was formed via **12c** [δ_P (C_6D_6) = 159.9]. Contrary to this reaction, an attempted thermal reaction of **12b** in toluene-d_8 in an NMR sealed tube at 127 °C for 1 h resulted in the recovery of **12b**. However, when the solid **12b** was heated at 180 °C (above its melting point) for 1 min, an intramolecular cyclization product **13b** [δ_P = 104, br.] was obtained almost quantitatively.



DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; R = 2,4-*t*-Bu_2-6-($MeSCH_2$)C_6H_2

The ^{31}P NMR chemical shifts for **12b,c** show upfield shifts, compared with that for the 2,4,6-tri-*t*-butylphenyl derivative **4** [δ_P ($CDCl_3$) = 298.2],[6a] by ca. 140 ppm. This fact suggests that there is a significant interaction between the phosphorus and the sulfur atoms and that contribution of intramolecularly coordinated form seems to be dominant as shown in the scheme below. It should be noted that the chemical shifts for **12b,c** exhibit downfield shifts, by ca. 10 ppm, compared with that for [2,4-di-*t*-butyl-6-(dimethylaminomethyl)phenyl]dithioxophosphorane (**14**) [δ_P ($CDCl_3$) = 149.6],[9d] indicating that the interaction between the phosphorus and the sulfur atoms in **12b,c** is less effective than that between the phosphorus and nitrogen atoms in **14**.



In fact, when **12b** was allowed to react with tris(dimethylamino)phosphine in benzene, formation of thioxophosphine **15b** [δ_P (C_6D_6) = 288.9] and 1,2-bis[2,4-di-*t*-butyl-6-(methylthiomethyl)phenyl]diphosphene [δ_P (C_6D_6) = 469.3], followed by conversion of **15b** to **16b**, was observed by ^{31}P NMR spectroscopic monitoring. The ^{31}P NMR chemical shift for **15b** is very similar to that for the [2,4-di-*t*-butyl-6-(dimethylaminomethyl)phenyl]thioxophosphine [δ_P (C_6D_6) = 282.7].[9e] It should be noted that an attempted desulfurization of a highly stabilized **14** using tris(dimethylamino)phosphine did not proceed.

The thioxophosphine **15b** was also generated from phosphonous dichloride **7b**. When **7b** was allowed to react with bis(trimethylsilyl) sulfide (1 equiv.) in THF in the presence of triethylamine (2 equiv.) at room temperature overnight, successive formation of **15b** and **16b** was observed during the reaction, being monitored by ^{31}P NMR spectroscopy. Finally, the compound **16b** was isolated in pure state in 36% yield after gel-permeation chromatography. **16b**: Colorless solid, mp 115–118 °C; δ_P ($CDCl_3$) = 89 (br.); FAB-MS *m*/*z* 623 (M^+–RPS–1), (molecular ion peak was not observed in the mass spectrum); MW (C_6H_6) 941±40.

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