## Reactivity of Carbanions Stabilized by Two Alpha Phosphorus Groups

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Abstract: The stabilized anion  $\{[Ph_2P(S)]_2CH\}^-$  with lithium as counter cation 1a reacts with formaldehyde or benzaldehyde to give vinylidene phosphine sulfides  $[Ph_2P(S)]_2C=CHR$ , where R is H or Ph, respectively (3, 4). The same anion with potassium as counter cation 1b gives vinyl phosphine sulfides (9-11). The formation of these two different classes of compounds is dependent on the the cation and the solvent used. The vinylidene phosphine sulfides can be reduced cleanly to produce the corresponding vinylidene tertiary phosphines 6 and 7.

Vinylidene tertiary phosphines **6** and **8** were synthesized for the first time by the reaction of lithium diphenylphosphide with vinylidene chloride and 1,1-dichloro-1-propene, respectively<sup>1,2</sup>. The resulting 1,1-bis(diphenylphosphino)ethene **6** and its derivatives<sup>1-7</sup> are important bidentate ligands<sup>2,8-11</sup> in coordination chemistry because the "bite" angle of these chelating ligands is sufficiently changed by the sp<sup>2</sup>-hybridized carbon so as to impart different coordination properties relative to those of their saturated counterparts such as 1,1-bis(diphenylphosphino)ethane or bis(diphenylphosphino)methane.

We have discovered a new synthetic route for vinylidene tertiry phosphine sulfides 3 and 4 and also a new synthesis of vinylidene tertiary phosphines 6 and 7 by reduction of the disulfides (Scheme 1). The stabilized anion { $[Ph_2P(S)_2CH]^-$  1a, prepared in benzene solvent from  $[Ph_2P(S)]_2CH_2$  and *n*-butyllithium, reacts with formaldehyde and benzaldehyde to produce the vinylidene phosphine sulfides 3 and 4 in yields of 58% and 54%, respectively. The reaction presumably proceeds via the putative intermediate 2a which loses LiOH to form the products. The <sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C NMR spectra and mass spectral data for 3 are identical to the earlier reported data<sup>4</sup>. The <sup>31</sup>P spectrum of 4, a new compound<sup>7,12</sup>, is an expected AX-type, with chemical shifts of 52.0(d) and 36.9(d) ppm and <sup>2</sup>Jpp of 32.8 Hz. The upfield resonance at 36.9 ppm is tentatively assigned, because of the  $\gamma$ -effect<sup>13</sup>, to the Ph<sub>2</sub>P(S)-group which is cis to the phenyl group. It has been demonstrated<sup>13</sup> that groups in the  $\gamma$ -position to phosphorus cause an unusually large upfield shift when in the cis position (e.g., in cis propenyl tertiary phosphines<sup>14,15</sup>) compared to the trans position.

This observed formation of vinylidene tertiary phosphine sulfides (in BuLi/benzene) is similar to the



\* ref. 2 (10%)

reactions of the carbanion (OC)<sub>4</sub>M[Ph<sub>2</sub>PCHPPh<sub>2</sub>]<sup>-</sup> which produces coordinated vinylidene phosphines upon reaction with ClCH<sub>2</sub>OCH<sub>3</sub> under certain conditions<sup>8</sup>. But it is in marked contrast to the previously reported work on the reaction of 1b with benzaldehyde in which the predominant products are vinyl or substituted vinyl phosphine sulfides<sup>16-18</sup> with no evidence of vinylidene compounds. However, the usual counter cations for these reactions were potassium or sodium in refluxing benzene or xylene. Similar reaction in THF using potassium t-butoxide as the base resulted in the formation of substituted vinyl phosphine sulfides (9-11) (Scheme 1). The formation of the vinyl phosphine derivatives appears to be the result of intramolecular attack of the alkoxide 2b on the more electropositive phosphorus leading to the fragmentation of the bisphosphine sulfide. Such an intramolecular attack does not seem to take place when Li<sup>+</sup> is the counter cation presumably because the alkoxide anion 2a is less naked when Li<sup>+</sup> is the counter cation than when K<sup>+</sup> is the counter cation. In other words to secure optimum yield of products, a non-polar solvent like benzene along with a cation such as lithium should be the choice to get vinylidene compounds, whereas a polar solvent like THF with a cation like potassium should be used to obtain vinyl compounds. When lithium is used in <u>THF</u>, the reaction is sluggish and gives poor yields of vinyl compounds.

Vinylidene tertiary phosphine sulfides **3** and **4** can be reduced following the method of desufurization of phosphinesulfides<sup>19,20</sup> with hexachlorodisilane to produce vinylidene tertiary phosphines **6** and **7** respectively. The phenyl derivative **7** is a new compound which has been characterized by its <sup>31</sup>P NMR and mass spectra.<sup>7,12</sup> The <sup>31</sup>P spectrum is two singlets at -2.6 and -10.7 ppm ( $^{2}J_{pp} < 1$  Hz). This negligible geminal P-P coupling in the phenyl compound is in contrast to values of 98 Hz and 7 Hz for the unsubstituted analog **6** and the methyl analog **8**, respectively. The small J-value for **8** compared to **6** has been explained<sup>2</sup> as due to conformational effects due to restricted rotation of the Ph<sub>2</sub>P-group cis to the methyl and orientation of the phosphorus lone pairs in opposite directions<sup>2,3,5</sup>. The larger phenyl group would cause a greater effect than methyl and thus the prediction of an even smaller J is reasonable for **7**.

General Experimental Procedures. (a) Vinylidene compounds. Dry thiophene free benzene (30 mL) along with 2.0g (4.46 mmol) of  $[Ph_2P(S)]_2CH_2$  1 were stirred vigorously with a magnetic stirrer under a nitrogen atmosphere. A 6.0 mL sample of *n*-BuLi (1.55 M / hexane, 9.3 mmol) was added via syringe. The reaction mixture turned yellow and was allowed to stir for 30 min. Benzaldehyde (1.0 mL, 9.8 mmol) in 5.0 mL of benzene was added dropwise over a ten minute period. The reaction mixture was allowed to stir at room temperature for three hours (for paraformaldehyde, reflux for four hours). The solvent was removed by rotary evaporation. The residue was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> and the lithium salts were extracted into water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was column chromatographed on silica gel (0-40% CH<sub>2</sub>Cl<sub>2</sub>/ hexane). Crystallization from a CH<sub>2</sub>Cl<sub>2</sub>/ ethanol mixture occurred during refrigeration for two days at 5°C to give pale yellow crystals of 4 (1.3g, 54% yield), melting point, 160°C.

(b) Olefination reactions in potassium t-butoxide/THF: The dichalcogenide compound,  $[Ph_2P(S)][Ph_2P(X)]CH_2$ , where X = S or O, (e.g. 1) was dissolved in dry, distilled THF. Potassium *tertiary*-butoxide (3 molar excess) was added and the reaction mixture was heated at 50°C for 30 min and then allowed to cool to room temparature. Benzaldehyde (3 molar excess) in THF was added over a ten minute period. Heating was not necessary for most of the dichalcogenide compounds, except in the case of reaction of dioxide with benzaldehyde (which was refluxed for two hours). The reaction is complete in less than five hours. With

heating, the reaction seems to be faster (complete in less than two hours). Only E- isomer was formed (9-11) both under ambient conditions and heating. The vinyl phosphine was extracted into  $CH_2Cl_2$  selectively leaving the other fragmentation product, the salt of diphenylthiophosphinic acid in the water layer during the work up. The vinyl phosphine sulfides usually were found to crystallize in  $CH_2Cl_2$  (ether / pentane mixture.

## **References and Notes**

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- 12. New compounds were characterized by <sup>31</sup>P and <sup>13</sup>C NMR (using a Bruker WP200 MHz instrument) and mass spectra . 4: <sup>31</sup>P NMR (in CDCl<sub>3</sub> with H<sub>3</sub>PO<sub>4</sub> as external ref ):  $\delta$  52.0(d), 36.9(d), <sup>2</sup>J<sub>PP</sub> = 32.8 Hz. <sup>13</sup>C NMR: (CDCl<sub>3</sub>):  $\delta$  159.3 (d), <sup>2</sup>J<sub>CP</sub> = 6.0 Hz, terminal C; geminal C not observed. Mass spectrum, *m/e* (relative intensity): 536(M<sup>+</sup>, 43), 504(48), 472(44), 427(53), 395(25), 363(27), 319(49), 262(100), 185(48), 183(75), 139(30), 108(19), 77(12). 7: <sup>31</sup>P NMR :  $\delta$  -2.6(s), -10.7(s), <sup>2</sup>J<sub>PP</sub>< 1 Hz. <sup>13</sup>C NMR:  $\delta$  152.9 (d), <sup>1</sup>J<sub>CP</sub> = 23.6 Hz;  $\delta$  136.0(dd), <sup>2</sup>J<sub>CP</sub> = 4.2, 12.5 Hz. Mass spectrum: 472 (M<sup>+</sup>, 88), 471(32), 287(19), 263(22), 262(100), 209(14), 186(26), 183(53), 108(61), 107 (26), 94(25), 77(3).
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