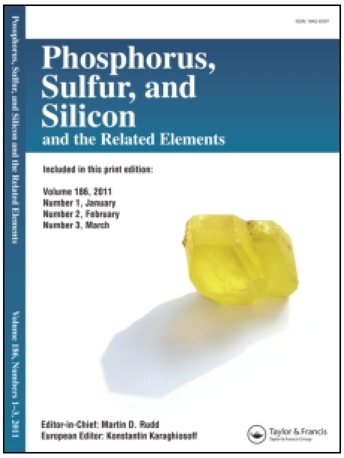

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The Reaction of α-Amino-Substituted Diphenylphosphine Oxides with Elemental Sulfur and Selenium. A New Route to Thio- and Selenoamides

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THE REACTION OF α-AMINO-SUBSTITUTED DIPHENYLPHOSPHINE OXIDES WITH ELEMENTAL SULFUR AND SELENIUM. A NEW ROUTE TO THIO- AND SELENOAMIDES.

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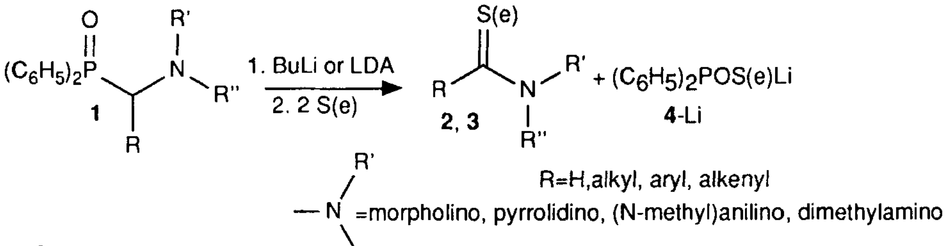
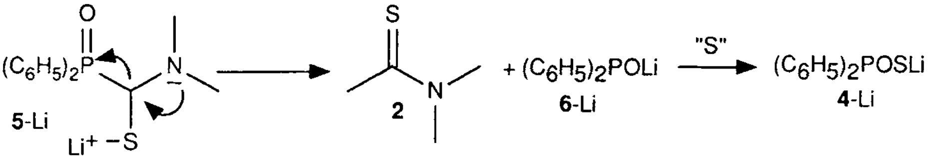
Lithiated α-amino-substituted diphenylphosphine oxides **1** showed an interesting reactivity towards sulfur and selenium, leading to the formation of thioamides **2** and selenoamides **3**, which could be isolated in good yields. Two equivalents of the chalcogene were found to be needed for complete conversion of the phosphine oxide anions. In the case of sulfur, diphenylphosphinothioic acid **4** was isolated as a side product, thus explaining the stoichiometry of the reaction (Scheme 1).

The optimal reaction conditions were found to depend both on the nature of the substituent R in **1** and on the chalcogene. If R=H, aryl or alkenyl, the reaction with sulfur was carried out routinely at 0°C. In the case of R=alkyl, deprotonation of the newly formed thioalkanamide by **1**-Li (R=alkyl), resulted in low yields. This deprotonation could be suppressed by lowering the temperature to -20°C. Markedly increased yields of thioalkanamide could be obtained. The reaction of **1**-Li with selenium required room temperature.



Scheme 1

The mechanism of the reaction of **1**-Li with sulfur was deduced from a ^{31}P NMR study. First, an α-phosphinoyl thiolate **5**-Li is formed. Thioamides **2** result from elimination of lithiated diphenylphosphine oxide **6**-Li from **5**-Li, triggered by the nitrogen lone pair. Subsequently, **6**-Li reacts with a second equivalent of sulfur to **4**-Li. The selenoamides are thought to be formed by a similar mechanism.



Scheme 2