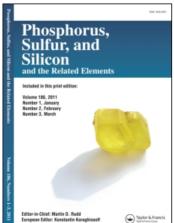
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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## A Facile and General Synthesis of Phosphinylguanidines

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#### A FACILE AND GENERAL SYNTHESIS OF PHOSPHINYLGUANIDINES

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Abstract: In order to synthesize new phosphorus guanidines 3, 5 as potential agrochemicals the reactivity of phosphorus cyanamides 1, 4, was investigated towards aliphatic and aromatic amines.

Sodium diphenylphosphinyl cyanamides 1 reacts with alkyl-, aryl-ammoniumchlorides under mild conditions to alkyl-, aryl-diphenylphosphinyl cyanamides 2, which rearrange, at temperature depending on the amine basicity, to give N-alkyl or (aryl) N'-diphenylphosphinyl guanidines 3<sup>1</sup>.

$$\begin{bmatrix} Ph_2P & X \\ NCN \end{bmatrix} Na^{+} \frac{RNH_3Cl}{(-NaCl)} \begin{bmatrix} Ph_2P & X \\ NCN \end{bmatrix} RNH_3 & \frac{R = Aryl}{T = 25^{\circ}C} Ph_2P & NH_2 \\ RNH_3 & \frac{T = 25^{\circ}C}{R = Alkyl} Ph_2P & N=C \\ T = 130-190^{\circ}C & 3 & NHR \\ X = O, S & (Yields : 65-95\%) & (Yields : 50-90\%)$$

Low temperature <sup>1</sup>H-NMR and X-Ray cristallographic investigations show that only one tautomeric form exist, in which the imino substituent is in  $\alpha$  position to the phosphorus atom.

This work was extended to the synthesis of phosphonioguanidines  $5^2$ .

$$R'Ph_{2}P = NCN \xrightarrow{RNH_{3}C1} \begin{bmatrix} R'Ph_{2}P - N = C & NH_{2} \\ CH_{3}CN \text{ Reflux} & SNH_{2} & CNH_{2} \\ 1 & NH_{3}CN & (R = Aryl) \\ 1 & (R' = Ph^{3}, R"NH) \\ 1 & (Yields: 50-85\%) \end{bmatrix}$$

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