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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

## The P(III) Thioacid Anhydrides Synthesis, Structure, Reactions

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**To cite this Article** Alfonsov, V. A., Pudovik, D. A., Batyeva, E. S., Pudovik, A. N. and Arbuzov, A. E.(1990) 'The P(III) Thioacid Anhydrides Synthesis, Structure, Reactions', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 175

To link to this Article: DOI: 10.1080/10426509008040709 URL: http://dx.doi.org/10.1080/10426509008040709

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THE P(III) THIOACID ANHYDRIDES. SYNTHESIS, STRUCTURE, REACTIONS

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The acetylthio- and acetimidoylthioderivatives of P(III) acids have been obtained in the reactions of thioacetamide and thioacetic acid, and their derivatives with different P(III) compounds containing groups that are easily detached. As a rule, the reactions proceed with the formation of S-phosphorylated derivatives and only very rarely can the X-phosphorylated compounds be obtained.

$$R_2PA + \begin{bmatrix} X & S \\ R'CSB \text{ or } R'CXB \end{bmatrix} \xrightarrow{-AB} R_2PSCR' + R_2PXCR'$$

The compounds of type I easily enter the nucleophilic substitution reactions to the P-atom with the rupture of the P-S bond and addition reactions to the C=O and C=N unsaturated bonds. While heated or affected, they also rearrange the alkyl- and acylhalides.

The X-ray crystal study has shown these compounds to have an unexpected molecular structure with a short intramolecular contact between the P(III) atom and terminal heteroatom of the acid residue. These distances are by 0.65-0.80 Å shorter than the sum of Van der Waals' radii.

$$\begin{array}{cccc}
X & & & \\
E & & & \\
X & & \\
X & & \\
X & &$$

The nature of this short contact is discussed.