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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

Bis(1,1,3-trihydroperfluoropropyl)isocyanato Phosphite and Tris(1,1,3-trihydroperfluoropropyl) Phosphite in Reactions with Carbonyl Compounds

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 $\label{this Article} \textbf{To cite this Article} \ Konovalova, I.\ V.\ , Burnaeva, L.\ A.\ , Khusnutdinova, E.\ K.\ and Pudovik, A.\ N. (1987) 'Bis(1,1,3-trihydroperfluoropropyl) Phosphite in Reactions with Carbonyl Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 781$

To link to this Article: DOI: 10.1080/03086648708079273 URL: http://dx.doi.org/10.1080/03086648708079273

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Bis(1,1,3-trihydroperfluoropropyl)isocyanato Phosphite and Tris(1,1,3-trihydroperfluoropropyl) Phosphite in Reactions with Carbonyl Compounds

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Nucleophilicity of (I) in reactions with such carbonyl compounds as chloral, benzyl, ester and nitrile of benzoylformic acid is found to be notably reduced by the electronoaccepting perfluoropropyl groups. Unlike of dialkyl isocyanatophosphites (I) afford the cycloaddition products with >P-N- fragment (II) which being unable for the imide-amide rearrangement undergo dimerization into crystalline cyclodiphosphazanes (III) with pentacovalent phosphorus atoms.

(CHF₂CF₂CH₂O)₂PNCO +
$$R^1$$
COR — (CHF₂CF₂CH₂O)₂ O (CHF₂CF₂CH₂O)₂ O R^1 C=O R^1 C=O R^1 C=O R^1 C=O (CHF₂CF₂CH₂O)₂ (III)

Reactions of dialkyl isocyanatophosphites with esters of acetoacetic, trifluoroacetoacetic acids and with hexafluoroacetylacetone may involve either C=O or C=C bond, being depended on constitution of β -dicarbonyl compound. Interaction of (I) and tris(1,1,3-trihydroperfluoropropyl)phosphite with esters of chloro-, bromopiruvic and trichloroacetylphosphonic acids results in the formation of the Perkov reaction products.