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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 Formation of Phosphacycloheptatrienes in Ring Enlargement Reaction Gy. Keglevich^a; I. Petnehazy^a; L. Tbke^a

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To cite this Article Keglevich, Gy., Petnehazy, I. and Tbke, L.(1990) 'The Formation of Phosphacycloheptatrienes in Ring Enlargement Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 273

To link to this Article: DOI: 10.1080/10426509008040807 URL: http://dx.doi.org/10.1080/10426509008040807

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THE FORMATION OF PHOSPHACYCLOHEPTATRIENES IN RING ENLARGEMENT REACTION

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The formation of substituted phosphacycloheptatrienes in ring expansion reaction(s) is described. From the reaction of 3,4-dimethyl-l-phenyl-3-phospholene-1-oxide($1, R^1 = C_6H_5, R_2 =$ R_3 =CH $_3$) with dichlorocarbene under liquid-liquid phase transfor circumstances not the expected adduct but the appropriate phosphacycloheptatriene $(4,R_1,R_2,R_3)$ as above) was prepared. The formation of this product can be explained assuming two ring expansions effected by two series of dichlorocarbene addition and cyclopropane ring opening. In the similar reaction of the methoxy-phospholene derivative $(1, R^1 = CH_3O, R^2 =$ \mathbb{R}^3 =CH $_3$) four other products are also formed beside the phosphacycloheptatriene. Again phosphacycloheptatrienes (4) are formed as the result of dichlorocarbene addition to the regioisomers of dihidrophosphorins (2) obtained from the phospholene-dichlorocarbene adducts by thermolysis. The same product can be derived from each regioisomeric pair.

$$1/R^{1}=C_{6}H_{5}, CH_{3}O$$
 $R^{2}=R^{3}=CH_{3}$

$$R^{2}=H$$
, $R^{3}=CH_{3}$
 $R^{2}=H$, $R^{3}=CH_{3}$
 $R^{2}=CH_{3}$
 $R^{2}=CH_{3}$
 $R^{2}=CH_{3}$
 $R^{2}=H$, $R^{3}=CH_{3}$
 $R^{2}=H$, $R^{3}=CH_{3}$