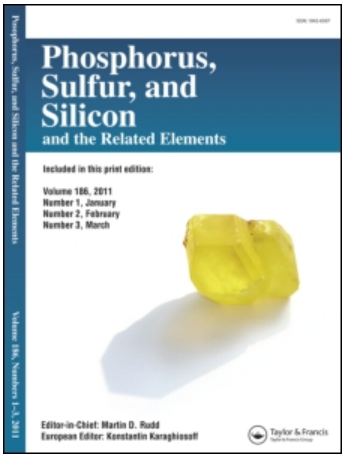

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Gy. Keglevich[a]; I. Petnehazy[a]; L. Tbke[a]
[a] Organical Chemical Technology Department, Technical University of Budapest,

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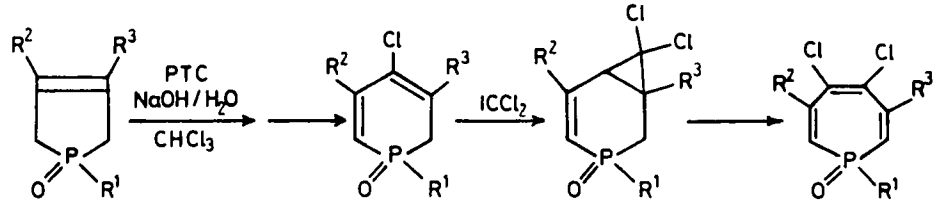
THE FORMATION OF PHOSPHACYCLOHEPTATRIENES IN RING ENLARGEMENT REACTION

Gy.KEGLEVICH, I.PETNEHÁZY, and L.TÖKE
Organical Chemical Technology Department, Technical University of Budapest

The formation of substituted phosphacycloheptatrienes in ring expansion reaction(s) is described. From the reaction of 3,4-dimethyl-1-phenyl-3-phospholene-1-oxide(1, $R^1=C_6H_5$, $R_2=R_3=CH_3$) with dichlorocarbene under liquid-liquid phase transfer 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, $R^1=CH_3O$, $R^2=R^3=CH_3$) 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/ $R^1=C_6H_5$, CH_3O
$R^2=R^3=CH_3$

2/ $R^1=n\text{-}C_3H_7$, $n\text{-}C_4H_9$, C_6H_5, CH_3O
$R^2=H$, $R^3=CH_3$ $\quad$ $R^2=H$, $R^3=CH_3$ $\quad$ $R^2=CH_3$, $R^3=H$ $\quad$ $R^2=H$, $R^3=CH_3$