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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>

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To cite this Article Keglevich, Gy. , Petnehazy, I. and Tuke, L.(1990) 'Ring Enlargement of Phospholenes to Phosphorin Derivatives Through Dichlorocarbene Adducts', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 274

To link to this Article: DOI: 10.1080/10426509008040808

URL: <http://dx.doi.org/10.1080/10426509008040808>

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RING ENLARGEMENT OF PHOSPHOLENES TO PHOSPHORIN DERIVATIVES THROUGH DICHLOROCARBENE ADDUCTS

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The ring enlargement of readily available phospholenes by dichlorocarbene addition to the double bond and subsequent opening of the cyclopropane ring is discussed. Adducts of phospholene with dichlorocarbene (2) can be synthesised under liquid-liquid phase transfer circumstances. The simplest way to open the cyclopropane ring in the adducts is thermal transformation giving the two regioisomers of the appropriate dihydrophosphorin (3). Electrophilic reagents can also be used for the opening of the cyclopropane ring. On heating with silver nitrate in water or in alcohols the adducts are transformed to the two regioisomers of the hydroxy- or the alkoxy - tetrahydrophosphorins, respectively (4, Y=H, CH₃, C₂H₅). In the reaction of adducts with mercury acetate-acetic acid the corresponding acetoxy-derivatives (4, Y=CH₃CO) are formed. The Friedl-Crafts reaction of the adducts with benzene in the presence of aluminium trichloride yields diarylated product.

