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The Interaction of Diazo Compounds with Phosphorylated Systems with S-H, S-S, S-Hal Bonds

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THE INTERACTION OF DIAZO COMPOUNDS WITH PHOSPHORYLATED SYSTEMS WITH S-H, S-S, S-Hal BONDS

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The interactions of phosphorylsulphenylhalides, phosphorylated disulphides, thio- and dithiophosphoric acids with diazo compounds were investigated. It has been shown that these reactions mainly lead to the insertion of methylene groups into S-Hal, S-S, S-H bonds. a-Chloromethyl-phosphorothio- and -dithioates are obtained from the corresponding phosphoryl- and thiophosphorylsulphenyl-chlorides. As for phosphorylsulphenylbromides, the reaction is accompanied by phosphoryl-thiophosphoryl rearrangements:

$$(RO)_{2}P \xrightarrow{X} + N_{2}CR'R^{2} \xrightarrow{X=0, S; Y=C1, Br} (RO)_{2}P - SCR'R^{2}$$

$$X=0, S; Y=C1, Br \rightarrow (RO)_{2}P - SCR'R^{2}$$

$$X=0; Y=Br \rightarrow (RO)_{2}P - XCR'R^{2}$$

Phosphorylated disulphides react with phenyl diazomethane forming the corresponding bis-phosphoryl-phenylmethanes. Bis-phosphoryl-diphenylmethanes are obtained only by the reaction of disulphides with diphenyl carbene formed from diphenyl dichloromethane by metallic lithium:

$$\begin{array}{c} \text{O(S)} & \text{O(S)} \\ \text{(RO)} & \text{2}^{\text{P-S-S-P}} \text{(OR)} \\ \text{2} \end{array} \xrightarrow{ \begin{array}{c} \text{(C$_{6}$^{\text{H}}$_{5}$)}$_{2}$CCl$_{2}$+$Li} \\ \text{(RO)} & \text{2}^{\text{P-S-C-S-P}} \text{(OR)} \\ \text{2} \end{array} \xrightarrow{ \begin{array}{c} \text{O(S)} & \text{C$_{6}$^{\text{H}}$_{5}$O(S)} \\ \text{(RO)} & \text{2}^{\text{P-S-C-S-P}} \text{(OR)} \\ \text{C$_{6}$^{\text{H}}$_{5}} \end{array} }$$

The insertion into S-H bond in the reaction of thio- and dithiophosphoric acids with bis-diazo ketones was studied:

$$(RO)_{2}^{O(S)} + \begin{bmatrix} 0 \\ N_{2}CHC - \end{bmatrix}_{2} Z \longrightarrow \begin{bmatrix} (RO)_{2}^{O(S)} & 0 \\ || (RO)_{2}^{O(S)} - || (RO)_{2}^{O(S)} -$$