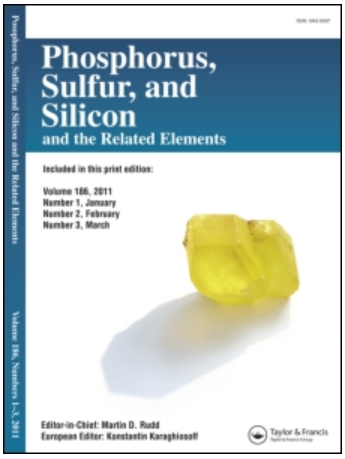


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# Phosphorylation of Nitrogen-Bearing Unsaturated and Aromatic Compounds

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# PHOSPHORYLATION OF NITROGEN-BEARING UNSATURATED AND AROMATIC COMPOUNDS

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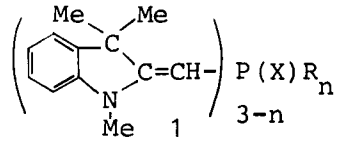
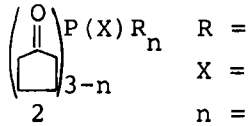
The enamine reaction provides a valuable method for the selective alkylation and acylation of aldehydes and ketones. Similar procedure of phosphorylation is not practically studied. Using 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) as the model enamine we investigated conditions of phosphorylation as well as stereochemistry, and reactions of obtained products of type 1. It was found that properties of some compounds were similar to those of amides of phosphorus acids (vinilologie).



1

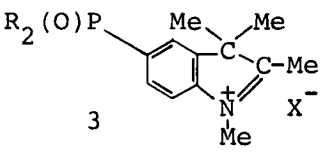
R = Cl,Br,Ar,Alk,OAlk,$NAlk_2$
X = lone pair, O,S,NR'
n = 0,1,2

These findings were used for synthesis of phosphorylated derivatives of other enamines and phosphorylated ketones of type 2.



2

R = Alk,Ar
X = O,S
n = 1,2



3

R = Et,Ph, OEt

1,2,3,3-Tetramethylindoline (reduced Fischer's base) is phosphorylated with $PCl_3$ or $PBr_3$ in benzene ring like N,N-dialkylanilines which are vinilogs of enamines. After a number of reactions, 5-substituted salts of 2-methyleneindoline of type 3 were obtained. Using those salts a number of phosphorylated cyanine dyes were synthesized in addition to the known series of phosphorylated dyes that permitted to elucidate the nature of auxochrome effect of phosphorus-bearing groups.