PREPARATION AND REACTIONS OF TRIVALENT SULFUR COMPOUNDS CONTAINING HETEROCYLCES

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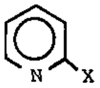
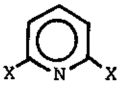
Recently, we found that methyl 2-pyridyl sulfoxide can be used as a good phase transfer catalyst which promotes the nucleophilic displacement reactions. In order to extend further this catalytic acitvity of organo sulfur compounds containing pyridine nuclei, we prepared several other 2-substituted and 2,6-disubstituted sulfides and sulfoxides[II]-[VII] and tested as phase transfer catalysts.

The pKa values for these compounds [II]-[VI] were measured by UV-technique. The pKa values of 2-substituted derivatives [I],[II],[III],[IV] together with those of other pyridine derivatives having substituents at α-position could be correlated well with Hammett-Taft σ*-values giving a good straight line of being $\rho^*=-4.4$. The σ*-values of 2-methylsulfenyl and 2-methylsulfinyl groups were calculated from the corresponding σ_I-values. The additivity rule of the substituent constant σ* is observed in 2,6-dimethyl pyridine while in the case of both 2,6-disubstituted sulfide[V] and sulfoxide[VI], this rule could not be applied probably due to steric reason. Especially, in the case of [VI] the calculated pKa value(0.80) is smaller than that of the observed value(1.53), suggesting that bis-sulfinyl group in [VI] can fix the proton by strong hydrogen-bonding.

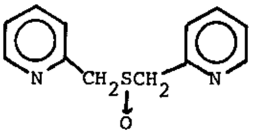
The sulfides, sulfoxides and sulfone [I]-[VII] were tested for phase-transfer catalysts. Among several reactions, as shown in Table 4, the sulfoxides [II],[IV],[VI],[VII] work as excellent phase transfer catalysts for the alkylations of active methylene compounds such as benzyl cyanide and benzyl methyl ketone with several alkyl halides under liquid-liquid two phase system. Furthermore, with these sulfoxides only the mono alkylation products were obtained except in the case of the reaction between benzyl cyanide and methyl iodide. Thus, these sulfoxides are expected to be able to use as good phase transfer catalysts with high selectivity.



	-X
[I]	$-SCH_3$
[II]	$-S(O)CH_3$
[III]	$-CH_2SCH_3$
[IV]	$-CH_2S(O)CH_3$



	-X
[V]	$-CH_2SCH_3$
[VI]	$-CH_2S(O)CH_3$



[VII]