ALKYLATION OF BENZOTHIAZOLINES AND THEIR STEVENS REARRANGEMENT

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2-Substituted N-methylbenzothiazolines were methylated with Meerwein reagents to give the cyclic ammonium salts, i.e., 2-substituted N,N-dimethylbenzothiazolinium salts.

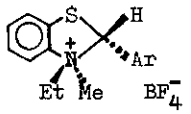
When the benzothiazolines were alkylated with triethyloxonium tetrafluoroborate, the resulting salts were a mixture of two stereoisomers (1-A and 1-B), and, in some cases (Ar = Ph and p-ClC_6H_4), pure salts of one isomer (1-A) were isolated by recrystalization from ethanol.

The selectivity of N- and/or S-alkylation of related compounds were examined with $R_3O^+BF_4^-$, MeI, and MeI/$AgClO_4$. When the nitrogen atom is not contained in resonance with a benzene ring, alkylation occurs solely on the nitrogen and when it is with two benzene rings, i.e., phenothiazine, alkylation takes place on the sulfur even with $R_3O^+BF_4^-$. Competition to alkylate N and S takes place when the nitrogen is connected to one benzene ring.

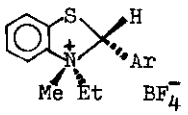
2-Aryl-3,3-dialkylbenzothiazolinium salts with lithium diisopropylamide (LDA) and butyllithium to give the Stevens rearrangement products of different types.

In the reactions with LDA, abstruction of a proton at C-2 took place to give π-type cyclic ammonium ylide (O) as an intermediate, which afforded the rearrangement product, i.e., 2,2-disubstituted N-methylbenzothiazoline in a moderate yield.

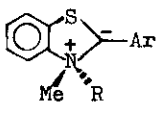
In the reactions with butyllithium, direct attack at the sulfur of the ring took place to give the ring-opened ammonium ylide (P), which afforded mainly unusual Stevens rearrangement product (2) by participation of ortho-butylthio group.



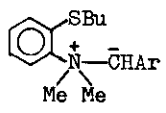
1-A



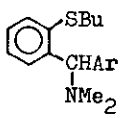
1-B



O R=Me,Et



P



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