

NOVEL REACTIONS OF BENZOTHAZOLINE DERIVATIVES

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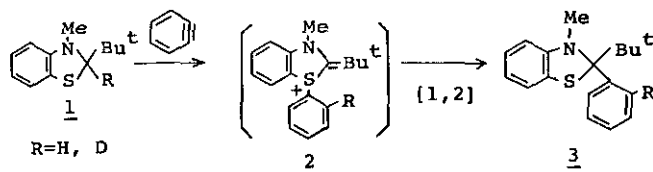
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A novel heterocyclic sulfur ylide, 2-t-butyl-3-methyl-1-phenylbenzothiazolinium ylide was recognized as a reaction intermediate, and novel ring transformation reactions of benzothiazoline sulfoxides and related compounds were investigated.

1. Reaction of 2-t-Butyl-3-methylbenzothiazoline with Benzyne--- Generation of 2-t-Butyl-3-methyl-1-phenylbenzothiazolinium Ylide

2-t-Butyl-3-methyl-1-phenylbenzothiazolinium ylide (2) was generated as an intermediate in the reaction of 2-t-butyl-3-methylbenzothiazoline (1) with benzyne. The ylide (2) underwent a novel intermolecular [1,2] shift to give 2-t-butyl-3-methyl-2-phenylbenzothiazoline (3).



2. Reactions of 3-Acetylbenzothiazoline 1-Oxides and Related Compounds with Acetic Anhydride

cis- and trans-Sulfoxides of 3-acetylbenzothiazoline, 3-acetyl-1,3-thiazolidine, 1,3-dithiolane, and 1,3-benzoxathiole underwent non-stereospecific ring expansions. These ring expansion reactions were explained by the mechanism involving the sulfenic anhydride intermediate resulted from the acetic anhydride-catalyzed ring-opening of the sulfoxides. On the other hand, cis-sulfoxides of 4-acetyl-2,3-dihydro-1,4-benzothiazine, 3-methyl-4-oxo-2,3-dihydro-1,3-benzothiazine, and 1- or 2-thiochroman were stereospecifically ring-expanded.