

NOVEL REACTIONS OF BENZOTHAZOLINE DERIVATIVES

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Novel ring transformation reactions of benzothiazoline derivatives were investigated.

1. Reactions of 3-Acetylbenzothiazoline 1-Oxides with Acetic Anhydride

2-Alkylsubstituted 3-acetylbenzothiazoline 1-oxides underwent ring expansions to yield 4-acetylbenzothiazines in good yield, upon treatment with acetic anhydride. The ring expansion proceeded equally well with either the cis or the trans isomers of the sulfoxides. This novel ring expansion is explained by the mechanism postulating the sulfenic anhydride intermediate resulted from the acetic anhydride-catalyzed ring-opening of the sulfoxides, followed by ring-closure.

2. Thermal Rearrangement Reactions of 3-Acetylbenzothiazoline 1-Oxides

Refluxing of 3-acetylbenzothiazoline 1-oxides in dry xylene caused ring expansions of the sulfoxides to give 4-acetylbenzothiazines in fairly good yield (30-60 %) and was accompanied by the formation of ring-opened products. The thermal ring expansion also proceeded equally well with the cis or the trans sulfoxides. Although the sulfoxides did not react in refluxing benzene, a vigorous reaction setted in as soon as a catalytic amount of benzoyl peroxide was added and resulted in the formation of ring expansion products, 4-acetylbenzothiazines. From these results, a possible pathway involving the radical intermediate is proposed for the ring expansion.

3. Reactions of 2,2-Disubstituted Benzothiazolines with Acid Anhydrides

Reaction of 2,2-disubstituted benzothiazolines with refluxing acetic anhydride for 3-5 hr afforded 2-acetylmethylenebenzothiazolines together with N-acetylated products. Similarly, from the reaction with propionic anhydride, 2-propionylmethylenebenzothiazolines were provided. A plausible mechanism of this novel transformation reaction is also discussed.