

SYNTHESIS AND PROPERTIES OF 1,3-THIAZINONES

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In connection with the ring-transformation reactions of 1,3-oxazin-4-ones recently reported from our laboratory, a variety of 1,3-thiazin-4-ones was required. This paper describes simple methods for preparation of 1,3-thiazinones from carboxamides or thiocarboxamides, and a few observed behaviors of the 1,3-thiazinones.

Various carboxamides smoothly underwent N-acetoacetylation by means of diketene-halosilane system to give the N-acetoacetyl derivatives in good yields. Acyl Meldrum's acids were also found to be effective for the N-acylacetylation.

The N-acylacetylcarboxamides were treated with perchloric acid or chlorosulfonic acid to form the intermediate 1,3-oxazinium salts, which were readily converted with H_2S into the corresponding 1,3-thiazin-4-ones in satisfactory yields. On the other hand, treatment of thiocarboxamides by way of diketene-halosilane system yielded 1,3-thiazin-4-ones and -6-ones.

The 2-alkyl-1,3-thiazin-4-ones were found to be readily hydrolyzed with acetone-water (1:1) leading to the ring-opened β -mercaptocrotonamide derivatives, whereas the 2-aryl-1,3-thiazin-4-ones did not undergo hydrolysis at the same condition.

Reduction of the 1,3-thiazin-4-ones with $NaBH_4$ or $LiAlH_4$ resulted in addition of hydrogen across the C=N double bond giving the corresponding 2,3-dihydro derivatives.

When the 2-alkyl-1,3-thiazin-4-ones (alkyl=Me, Et, n-Pr) were allowed to stand at room temperature overnight, the thiazinones were converted into the dimers (1).

Furthermore, treatment of these thiazinones with trifluoroacetic acid or chlorosulfonic acid gave rise to the dimers (2) of another type.

