SYNTHESIS AND CHEMICAL CHARACTERISTICS
OF 2-SUBSTITUTED THIAZOLINE-4,5-DIONES. (REVIEW)

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Methods for the production of 2-substituted thiazoline-4,5-diones and their thermolysis in the presence of nucleophiles and dienophiles are examined.

Keywords: 2-arylthiazoline-4,5-diones, azaheterocycles, thioaroyl isocyanates, nucleophilic addition, cycloaddition.

In most chemical transformations 2-substituted thiazoline-4,5-diones 1 form intermediate thioacyl isocyanates 2, which enter readily into nucleophilic addition and cycloaddition. Compounds 1 are heteroanalogs of 5-aryl-2,3-dihydrofuran-2,3-diones 3, which form a different type of acylheterocumulenes, i.e., the aroylketenes 4.

\[
\begin{align*}
\text{Ar} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{N} & \quad \text{C} = \text{O} \\
\text{Ar} & \quad \text{O} \\
\text{O} & \quad \text{Ar} \\
\text{N} & \quad \text{C} = \text{O} \\
\text{Ar} & \quad \text{O} \\
\text{O} & \quad \text{Ar} \\
\end{align*}
\]

\[\Delta \rightarrow \text{CO} \]


In spite of the structural similarity of compounds 1 and 3 their chemical characteristics have substantial differences arising from thermolysis, decyclization, and recyclization of both types of dioxoheterocycle [1]. Thiazolinediones 1 were first described in 1960 [2], and furandiones 3 were described in 1975 [3]. In contrast to the latter, however, there have not so far been any systematic data on compounds 1. Diones of type 1 were only briefly mentioned in reviews during examination of the chemical transformations of acylheterocumulenes [5], azadienes [6], and cyanamides [7].
1. THE PRODUCTION OF THIAZOLINE-4,5-DIONES

The first examples of thiazoline-4,5-diones were obtained with yields of 70-83% by the acylation of thioamides (mostly arylthioamides) with oxalyl chloride in absolute acetone at -20°C [2, 8-10].

\[
\begin{align*}
\text{R} & \quad \text{NH}_2 \quad \text{S} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{R} \quad \text{(COCl)}_2 \\
\end{align*}
\]

\[R = \text{Ph}, 4-\text{MeC}_6\text{H}_4 [2], 4-\text{ClC}_6\text{H}_4, 4-\text{O}_2\text{NC}_6\text{H}_4, 4-\text{MeOC}_6\text{H}_4, 4-\text{Me}_2\text{NC}_6\text{H}_4 [8],
2,4-\text{Me}_2\text{C}_6\text{H}_3, 2,4,6-\text{Me}_3\text{C}_6\text{H}_2 [9], \text{Ph}_2\text{CH}, \text{Br}, \text{Ph(EtOCO)CH}, \text{EtOCOCH}_2 [10]
\]

The corresponding 2-\text{tert-butyl}-, 2-styryl-, and 2-(1-naphthyl)thiazoline-4,5-diones 5-7 were obtained by an analogous procedure from \text{tert-butyl}-, styryl-, and naphthylthioamides [8, 9].

With oxalyl chloride in chloroform at -15 to -20°C the amides of dithiocarboxylic acids form 2-alkyl(aryl)mercaptothiazoline-4,5-diones 8 [11].

\[
\begin{align*}
\text{RS} & \quad \text{NH}_2 \quad \text{S} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{RS} \quad \text{(COCl)}_2 \\
\end{align*}
\]

\[R \quad \text{(yield of 8, %): Me (15), PhCH}_2 (86), \text{Ph (87)}
\]

During the production of 2-alkyl-, 2-phenyl-, and 2-cyclohexyloxythiazoline-4,5-diones 9 methylene chloride or dichloroethane was used instead of acetone. The reaction was conducted at 0°C [12].

\[
\begin{align*}
\text{RO} & \quad \text{NH}_2 \quad \text{S} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{RO} \quad \text{(COCl)}_2 \\
\end{align*}
\]

\[R = \text{Me, Et, Ph, cyclo-C}_6\text{H}_{11}
\]

2-Amino-substituted thiazoline-4,5-diones 10 are obtained with good yields from \text{N,N}-disubstituted thioureas in anhydrous ethyl acetate in the presence of triethylamine at -30°C [12].

\[
\begin{align*}
\text{RR'} & \quad \text{NH}_2 \quad \text{S} \quad \text{N} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{RR'} \quad \text{(COCl)}_2 \\
\end{align*}
\]

\[R, R' \quad \text{or} \quad R+R' \quad \text{(yield of 10, %): Me, Me (50); Et, Et (71); (CH}_2)_3 (73); \\
\text{Me, Ph (73); Et, Ph (73); Bu, Ph (65); Ph, Ph (75)}
\]