FORMATION OF 1,4,2-OXATHIAZOLE DERIVATIVES
IN THE REACTION OF 3-AMINO-2-ARYLINDENE-1THIONES WITH NITRILE n-OXIDES

N. A. Korchevin, V. A. Usov,

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A. F. Tokareva, and M. G. Voronkov

We have found that 3-amino-2-arylindene-1-thiones (I) react readily at 20-25° C with aromatic nitrile N-oxides to give spiran 1,4,2-oxathiazoles (II).

$$\begin{array}{c|c}
 & Ar - CNO \\
\hline
& S \\
& Ar - C \\
& S \\
& Ar - C \\
& S \\
& Ar - C \\
& S \\
& O \\
& R \\
& (-ArNCS)
\end{array}$$

$$\begin{array}{c}
 & NR^1R^2 \\
& (-ArNCS)
\end{array}$$

$$\begin{array}{c}
 & NR^1R^2 \\
& (-ArNCS)
\end{array}$$

 $\begin{array}{lll} \textbf{a} & R^{1}, & R^{2} = CH_{4}; & R^{3}, & Ar = C_{6}H_{5}, & \textbf{b} & R^{1}, & R^{2} = -\left(CH_{2}\right)_{5} -; & R^{3} = \alpha \cdot C_{10}H_{1}; & Ar = C_{6}H_{5}; & \textbf{C} & R^{1}, & R^{2} = c_{6}H_{5}; & Ar = p \cdot NO_{2}C_{6}H_{4} \end{array}$

Spiro[(3'-dimethylamino-2'-phenylindene)-1'-5-(3-phenyl-1,4,2-oxathiazole)] (IIa), with mp 117-118° (dec.), was obtained in 82% yield. Found: C 74.9; H 5.4; S 8.3%. $C_{24}H_{20}N_2OS$. Calculated: C 75.6; H 5.4; S 8.3%; Spiran IIb, with mp 126-127° (dec.), was obtained in 45% yield. Found: C 78.4; H 5.5; S 6.6%. $C_{31}H_{26}N_2OS$. Calculated: C 78.5; H 5.5; S 6.7%; Spiran IIc, with mp 142-143° (dec.), was obtained in 94% yield. Found: C 69.0; H 4.9; S 6.5%. $C_{27}H_{23}N_3O_3S$. Calculated: C 69.1; H 4.9; S 6.8%.

The IR spectra of II contain bands of stretching vibrations of C=N bonds (1610-1615 cm⁻¹), C=C bonds in a 5-membered ring (1560 cm⁻¹), and C=C bonds of aromatic rings (1580-1600 and 1480-1500 cm⁻¹).

When II is refluxed in dioxane it undergoes cleavage to give 3-amino-2-arylindene-1-one (III) and traces of enaminothione I. In piperidine, the latter is the chief product.

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