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

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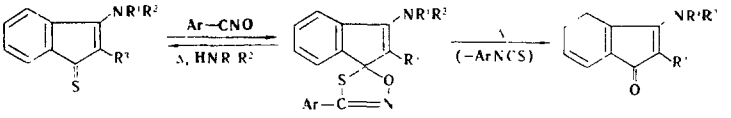
We have found that 3-amino-2-arylindene-1-thiones (I) react readily at 20-25° C with aromatic nitrile N-oxides to give spiran 1,4,2-oxathiazoles (II).



I II III

a R^1, $R^2=CH_3$; R^3, $Ar=C_6H_5$, b R^1, $R^2=-(CH_2)_5-$; $R^3=\alpha$-$C_{10}H_7$; $Ar=C_6H_5$; c R^1, $R^2=-(CH_2)_5-$, $R^3=C_6H_5$; $Ar=p$-$NO_2C_6H_4$

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 75.0; 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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