

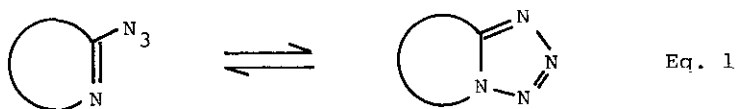
SYNTHESIS OF 5H-1,2,3-DITHIAZOLE, A NOVEL HETEROCYCLE

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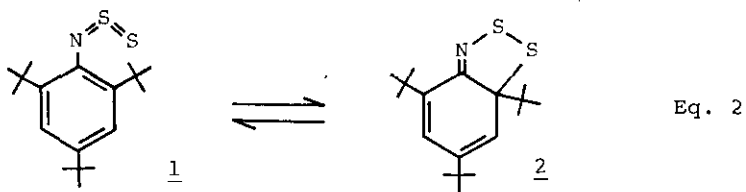
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Abstract The reaction of β -ketoenamines with disulfur dichloride afforded 5H-1,2,3-dithiazoles probably via cyclization of intermediate N-thiosulfinylamine. Implication of this reaction with the Herz reaction is also mentioned.

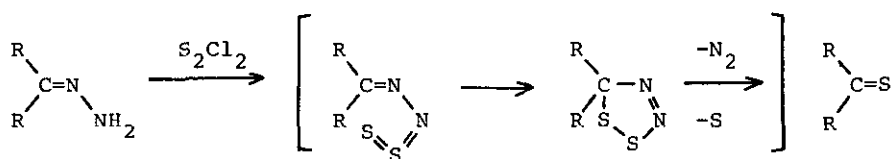
Azido-azomethine-tetrazole equilibrium has been extensively studied, especially in the field of azaheterocyclic systems (Eq. 1).¹



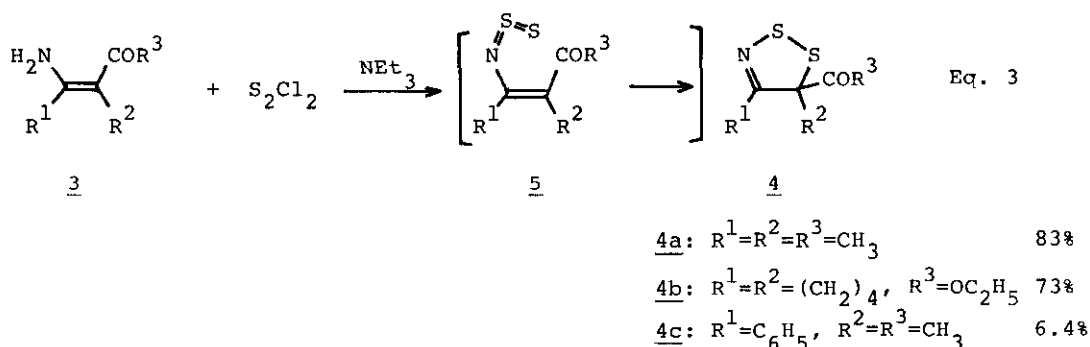
We recently described a similar chain-ring tautomerism for a new type of S(IV)-thiocumulene, N-thiosulfinylaniline (1) (Eq. 2) which was prepared from the reaction of the corresponding aniline with disulfur dichloride.² The compound (1) is equilibrated with a cyclized form (2) in solution, while in the solid state 1 exists only as the cyclized form (2).



We also communicated that the reaction of hydrazones with disulfur dichloride led to thioketones and it probably proceeded via cyclization of intermediate N-thiosulfinylamine followed by loss of nitrogen and sulfur.³



We now report a general method for the synthesis of 5H-1,2,3-dithiazole (4) by the reaction of β -ketoenamine (3)⁴ with disulfur dichloride (Eq. 3).



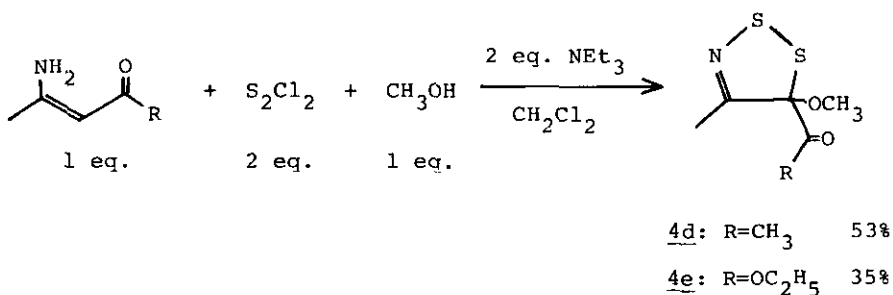
The reaction of 4-amino-3-methyl-3-penten-2-one (3, $R^1=R^2=R^3=CH_3$) with disulfur dichloride in dichloromethane with triethylamine as base gave 5-acetyl-4,5-dimethyl-5H-1,2,3-dithiazole (4a) in 83% yield.

Similarly, 1-amino-2-ethoxycarbonyl-1-cyclohexene (3, $R^1=R^2=(CH_2)_4, R^3=OC_2H_5$) and 4-amino-3-methyl-4-phenyl-3-buten-2-one (3, $R^1=C_6H_5, R^2=R^3=CH_3$) afforded the corresponding 5H-1,2,3-dithiazoles (4b and 4c) in 73 and 6.4% yields, respectively.

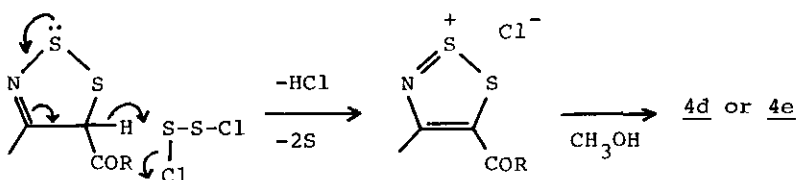
The structure of these dithiazoles was established by spectral and analytical data. For these heterocycles, unlike the case of Eq. 2, no evidence for the presence of open-chain isomer (5) was obtained by the NMR and electronic spectra. For example, 4a is a yellow oil (b.p. 83 °C/6 mmHg) with λ_{max} 390 nm (ϵ 380) and shows three singlets (in carbon tetrachloride, δ 1.68, 1.97, and 2.31) with equal intensity in the NMR spectrum; if the open-chain form (5a) were in equilibrium with 4a, a strong absorption characteristic of the N=S=S group (λ_{max} 540 nm) would be observed.²

In light of the equilibrium between 1 and 2, the above reactions probably proceed via cyclization of intermediate N-thiosulfinylamine (5) (Eq. 3).

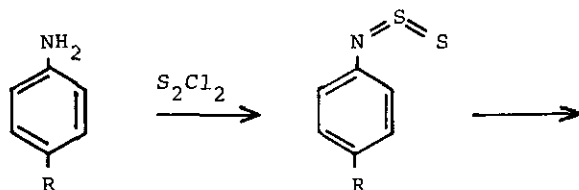
When a similar reaction was carried out for β -ketoenamine bearing β -hydrogen (3, $R^2=H$), the corresponding 5H-1,2,3-dithiazole was not obtained. However, the reaction in the presence of methanol resulted in the formation of methoxy substituted 5H-1,2,3-dithiazoles (4d and 4e) as shown below.

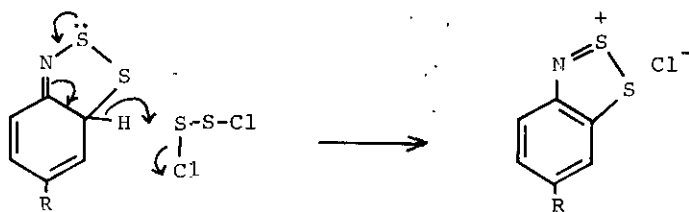


The formation of 4d and 4e can reasonably be explained by the following scheme involving a dithiazolium ion.



This reaction is interesting not only because it provides a preparative method of functionalized 5H-1,2,3-dithiazole but also because it sheds light on the mechanism of the Herz reaction (the formation of benzodithiazolium chloride by the reaction of aniline with disulfur dichloride).⁵ In view of the above findings as well as the equilibrium between 1 and 2 found by us, the formation of the benzodithiazolium salt can be accounted for by the following mechanism.





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4. The β -ketoenamines used in the present study were prepared by the method of Kolek and Leschinsky. J. A. Kloek and K. L. Leschinsky, J. Org. Chem., 1978, 43, 1460.
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