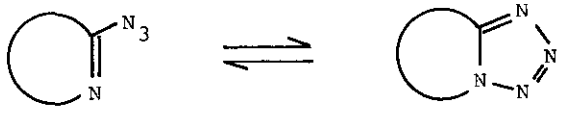
SYNTHESIS OF 5H-1,2,3-DITHIAZOLE, A NOVEL HETEROCYCLE

Renji Okazaki, Kaoru Inoue, and Naoki Inamoto*
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

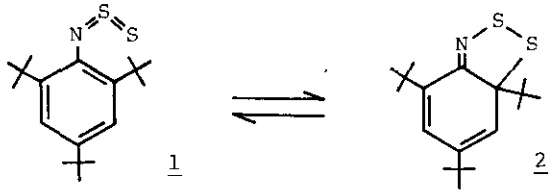
Abstract The reaction of β-ketoenamines with disulfur dichloride afforded 5H-1,2,3-dithiazoles probably via cyclization of intermediate N-thiosulfinylamine. Implication of this reaction with the Herz reaction is also mentioned.

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



Eq. 1

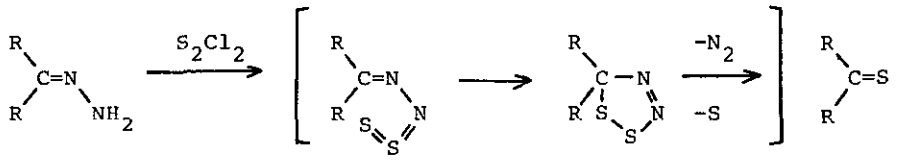
We recently described a similar chain-ring tautomerism for a new type of S(IV)-thiocumulene, N-thiosulfinylaniline (1) (Eq. 2) which was prepared from the reaction of the corresponding aniline with disulfur dichloride.[2] The compound (1) is equilibrated with a cyclized form (2) in solution, while in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



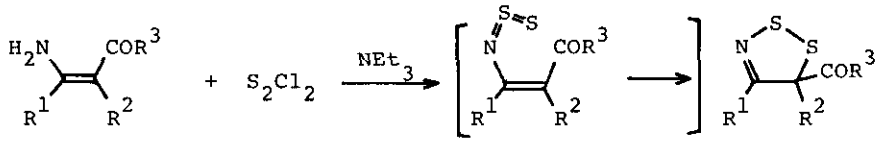
1 2

Eq. 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).



Eq. 3

3 5 4

4a: $R^1=R^2=R^3=CH_3$ 83%

4b: $R^1=R^2=(CH_2)_4$, $R^3=OC_2H_5$ 73%

4c: $R^1=C_6H_5$, $R^2=R^3=CH_3$ 6.4%

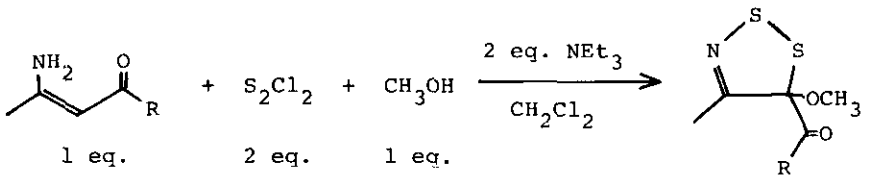
The reaction of 4-amino-3-methyl-3-penten-2-one (3, $R^1=R^2=R^3=CH_3$) with disulfur dichloride in dichloromethane with triethylamine as base gave 5-acetyl-4,5-dimethyl-5H-1,2,3-dithiazole (4a) in 83% yield.

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).

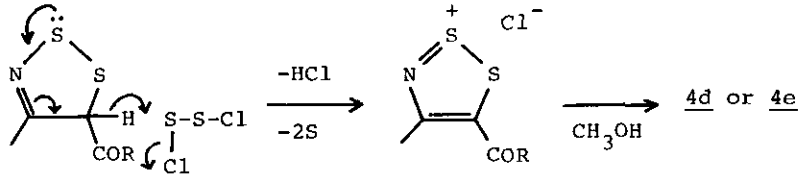
When a similar reaction was carried out for β-ketoenamine bearing β-hydrogen (3, R^2=H), the corresponding 5H-1,2,3-dithiazole was not obtained. However, the reaction in the presence of methanol resulted in the formation of methoxy substituted 5H-1,2,3-dithiazoles (4d and 4e) as shown below.



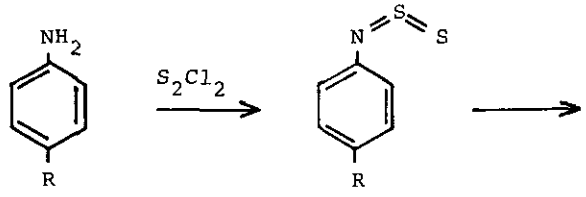
4d: R=CH_3 53%

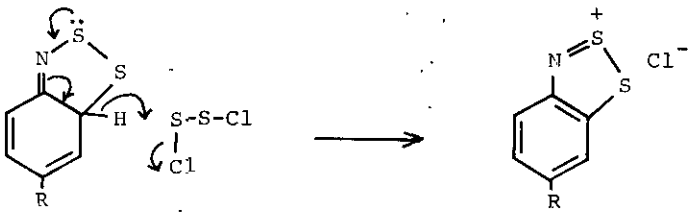
4e: R=OC_2H_5 35%

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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3. R. Okazaki, K. Inoue, and N. Inamoto, Tetrahedron Lett., 1979, 3673.
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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