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PREPARATION OF Δ^4-1,2,4-THIADIAZOLINE DERIVATIVES USING N-HALOAMIDINES[1)]

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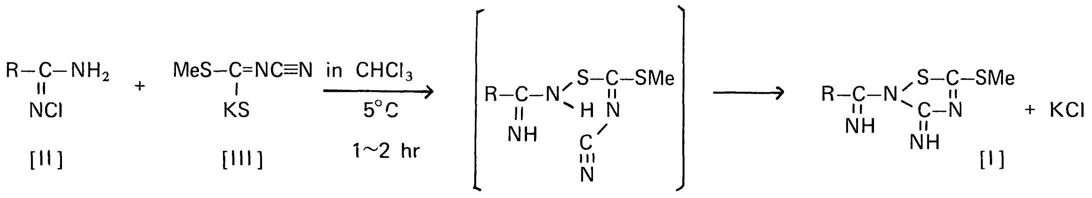
2-Imidoyl-3-imino-5-methylthio-Δ^4-1,2,4-thiadiazolines [I] were easily prepared by the reaction of N-chloroamidines [II] with potassium methyl cyanoiminodithiocarbonate [III]. By reduction, [I] was readily cleft at the N-S link and was recyclized to two kinds of s-triazines, and by alkaline hydrolysis, [I] was converted into 2-amino-4-hydroxy-s-triazine.

In a previous paper,[2)] we reported that N-alkylhaloamidines were treated with sodium alkoxide to form the corresponding O-alkylisoureas and that in these reactions, N-haloamidine released a halide ion after removal of a proton from amino group by alkoxide ion.

In this communication, it is described that direct replacement of the halogen atom of [II] by potassium methyl cyanoiminodithiocarbonate [III] has been examined and new heterocyclic compounds [I] have been obtained.



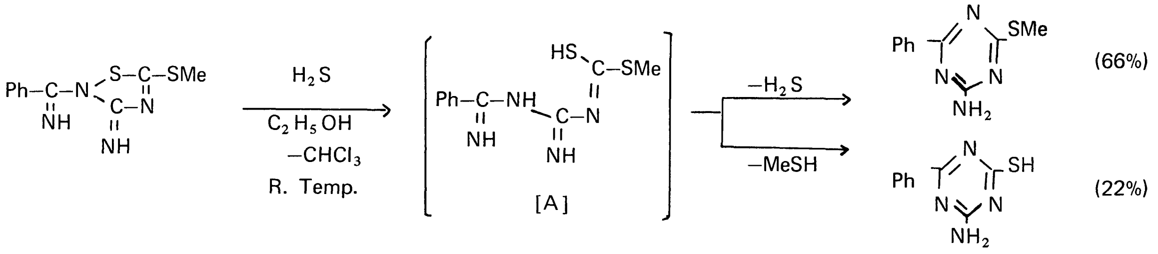
For example, to a stirred mixture of [III] (5.95 g, 0.035 mol) and chloroform (55 ml) was gradually added dropwise a solution of N-chloro-p-toluamidine (5.90 g, 0.035 mol) in chloroform (55 ml). The temperature was maintained below 5°C during the reaction. After about 2 hours of continued stirring, an active chlorine disappeared and potassium chloride precipitated. After the salt was removed by filtration, the filtrate was concentrated. Washing the residue with a little acetone afforded [I-a] (R = p-MeC_6H_4, 4.90 g, 53%, mp 175~178°C). Recrystallization from acetone gave a pure product, mp 181~182°C. To the washings was added a methanolic solution of cupric chloride. The cupper salt of [I-a] precipitated was collected by filtration, dp 253°C. The yield was 5%.

The structure of [I-a] was confirmed by elemental analysis, IR and mass spectra. Its IR spectrum showed $>$NH stretching band at 3350 cm^{-1} and 3200 cm^{-1} and $>$C=N– at 1650 cm^{-1} and 1630 cm^{-1}. In the mass spectrum, the parent peak, m/e 264, and other fragment peaks appeared appropriately. The structure of cupper salt consisting of [I] and $CuCl_2(H_2O)$ has not been established yet. In a similar manner, the other N-chloroamidines afforded the corresponding products [I].

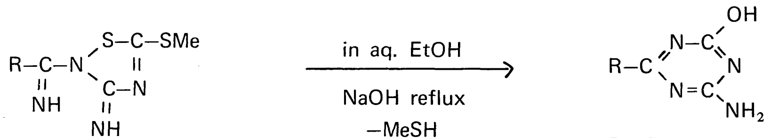
Table I. Physical properties of [I] and cupper salts

R	Yield (%)	[I] Mp (°C) Free Base	[I] Mp (°C) Picrate	UV Spectra $\lambda_{max}^{H_2O}$ ($\varepsilon \times 10^{-4}$)	Cupper Salt [I]. $CuCl_2(H_2O)_n$ Dp (°C)	Color	n
Ph	64	138~139	192~194 (dp)	256 (3.2)	246	Yellowish green	1
p–MeC_6H_4	58	181~182	204~205 (dp)	263 (3.5)	253	Green	1
$PhCH_2$	57	148~149 (dp)	183~185 (dp)	247 (2.8))	172~174	Dark blue	2
CH_3	58	155~158		243 (2.3)	–	–	–

[I] was readily cleft at the N-S link by hydrogen sulfide under a mild condition, and the elimination of methanethiol or hydrogen sulfide from intermediate [A] formed gave two kinds of s-triazines.



The ring cleavage of [I] by alkaline hydrolysis gave rise to triazine also. We found that [I] was converted into 2-amino-4-hydroxy-s-triazine with evolution of methanethiol. But the mechanism for this transformation has not yet been made clear.



R = Ph Yield 85%
p–MeC_6H_4 64%

The low stability of thiadiazolines seems to be related to the structure in which the aromatic character is absent.

Details will be published in our later paper.

Reference

1) N-Halo Compounds of Cyanamide Derivatives. II
(Part LXXXVI of "Studies of Cyanamide Derivatives")
2) T. Fuchigami, E. Ichikawa, and K. Odo, Bull. Chem. Soc. Japan., **46** 1765 (1973).

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