# Studies of the Chemistry of Azole Derivatives. VII. *N*-Substituted-2-amino-5-ketothiazolidino[4,5-*d*]thiazoles

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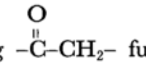
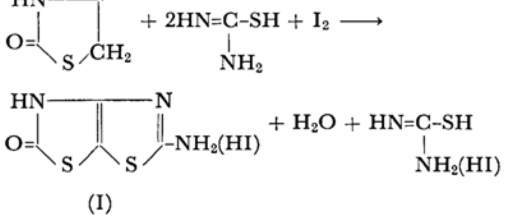
In extension to our previous work on thiazoles[2,3] the present communication deals with the study of reaction of compounds having



$-\overset{\overset{O}{\|}}{C}-CH_2-$

function in cyclic structure with lodine and monosubstituted thioureas. Dodson[4] reported the preparation of 2-amino-4-methyl-5-carbethoxythiazole by the reaction of acetoacetic ester, iodine and thiourea. In order to extend the application of this reaction, 2,4-diketothiazolidine was condensed with thiourea and iodine (1 : 2 : 1). The reaction can be represented as given below.



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On treatment with ammonium hydroxide (1) afforded the free base which could be diazotised using phosphoric acid and on acetylation it gave

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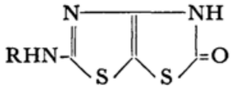
[1] Present address: Scientific Officer, Defence Science Laboratory, Delhi-6, India.

[2] J. M. Singh, *Can. J. Chem.*, in press.

[3] J. M. Singh and G. R. Chaudhry, *J. Indian Chem. Soc.*, **43**, 273 (1966).

[4] R. M. Dodson and W. King, *J. Am. Chem. Soc.*, **67**, 2242 (1945).

Table 1. *N*-Substituted-2-amino-5-ketothiazolidino[4,5-*d*]thiazoles



| Sample | R | Yield % | Mp °C | Molecular formula | N% Found | N% Colcd | S% Found | S% Calcd |
|---|---|---|---|---|---|---|---|---|
| 1 | Phenyl- | 41 | 200 | $C_{10}H_7N_3OS_2$ | 16.72 | 16.87 | 25.54 | 25.73 |
| 2 | *o*-Tolyl- | 35 | 190 | $C_{11}H_9N_3OS_2$ | 15.99 | 15.97 | 24.65 | 24.71 |
| 3 | *p*-Tolyl- | 39 | 195 | $C_{11}H_9N_3OS_2$ | 15.85 | 15.92 | 24.59 | 24.71 |
| 4 | *p*-Chlorophenyl- | 40 | 176 | $C_{10}H_6ClN_3OS_2$ | 14.72 | 14.81 | 22.35 | 22.57 |
| 5 | *p*-Bromophenyl- | 45 | 250 | $C_{10}H_6BrN_3OS_2$ | 12.65 | 12.80 | 19.39 | 19.51 |
| 6 | 2,4-Dichlorophenyl- | 40 | 300 | $C_{10}H_5Cl_2N_3OS_2$ | 13.06 | 13.26 | 20.31 | 20.13 |
| 7 | *α*-Naphthyl- | 35 | 220 | $C_{14}H_9N_3OS_2$ | 14.25 | 14.05 | 21.32 | 21.45 |
| 8 | *β*-Naphthyl- | 35 | 190 | $C_{14}H_9N_3OS_2$ | 14.13 | 14.05 | 21.35 | 21.45 |
| 9 | *p*-Nitrophenyl- | 30 | 160 | $C_{10}H_6N_4O_3S_2$ | 19.25 | 19.05 | 21.58 | 21.77 |
| 10 | *o*-Nitrophenyl- | 34 | 185 | $C_{10}H_6N_4O_3S_2$ | 19.19 | 19.05 | 21.68 | 21.77 |

monoacetylated derivative. These reactions, supported by analysis, confirmed the presence of an amino group.

Monosubstituted thioureas were prepared and condensed with 2,4-diketothiazolidine in presence of iodine (2 : 1 : 1) to give, *N*-substituted-2-amino-5-ketothiazolidino[4,5-*d*]thiazoles.

## Experimental

Substituted thioureas were prepared following the method of De Clermont.⁶⁾

2-Amino-5-ketothiazolidino[4,5-*d*]thiazole.

A mixture of 2,4-diketothiazolidine (0.1 mol), iodine (0.1 mol) and thiourea (0.2 mol) was heated on a water bath for 20 hr. The condenser was removed and heating was continued for another 12 hr. It was then kept in contact of ether for 12 hr. The excess of iodine was removed by sodium thiosulfate solution. 2-Amino-5-ketothiazolidino[4,5-*d*]thiazole hydroiodide thus formed was dissolved in water and neutralized with ammonium hydroxide solution to liberate the free base, recrystallized from alcohol, mp 175—177°C.

Found: N, 24.34; S, 36.35%. Calcd for $C_4H_3N_3S_2O$: N, 24.27; S, 36.99%.

The mono acetyl derivative melted at 220°C after recrystallization from benzene.

Found: N, 20.31; S, 30.31%. Calcd for $C_6H_5N_3S_2O_2$: N, 19.54; S, 29.76%.

Following this procedure other compounds were prepared.⁷⁾ Data of these products are listed in the table.

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5) K. Ganapthai and Venkataraman, *Proc. Indian Acad. Sci.*, **224**, 359 (1945).

6) Ph. De Clermont and E. Wehrlin, *J. Chem. Soc.*, **31**, 70 (1877).

7) All melting points are uncorrected and ethanol was used for recrystallization.