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SOME NEW HETEROCYCLIC SYSTEMS DERIVED FROM 6,7-DIAMINOBENZOTHIAZOLE

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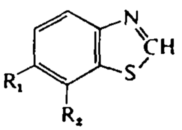
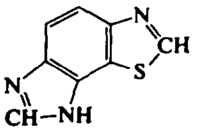
Abstract—Some new heterocyclic systems derived from 6,7-diaminobenzothiazole are reported, namely 8H-imidazo[4,5-g]benzothiazole, thiazolo[4,5-g]benzotriazole, and thiazolo[4,5-g]-2,1,3-benzoselenadiazole.

AROMATIC *o*-diamines undergo facile condensation reactions to give various five- and six-membered heterocyclic rings. 6,7-Diaminobenzothiazole (VII) was obtained from benzothiazole (I) by the stages indicated, and the authenticity of this compound demonstrated by the production of a phenazine derivative on treatment with phenanthraquinone.

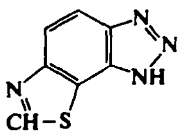


I, $R_1 = R_2 = H$.
II, $R_1 = NO_2$. $R_2 = H$.
III, $R_1 = NH_2$. $R_2 = H$.
IV, $R_1 = NH\,Tos$. $R_2 = H$.
V, $R_1 = NH\,Tos$. $R_2 = NO_2$.
VI, $R_1 = NH_2$. $R_2 = NO_2$.
VII, $R_1 = R_2 = NH_2$.

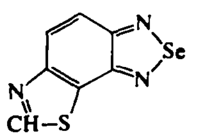
It was further characterized by conversion to imidazole, triazole, and selenadiazole ring systems.



VIII



IX



X

EXPERIMENTAL

Preparation of 6,7-*diaminobenzothiazole*. Compound II was obtained as the predominant isomer on nitration of I[1] and was readily reduced with $SnCl_2$ in HCl (method as for 6-nitro-1,2,3-benzothiadiazole[2] with slight modifications[3]) to III. The preparation of IV and its nitration have been described previously,[3] the procedure used being that employed for the corresponding derivatives of 1,2,3-benzothiadiazole.[2,4] The nitro-amide (V) was hydrolysed with conc. H_2SO_4 to give 7-*nitro*-6-*aminobenzothiazole* (VI), m.p. 224° from glacial AcOH. (Found: C, 43·0; H, 2·7. $C_7H_5N_3O_2S$ requires: C, 43·1; H, 2·6%), and on reduction with $SnCl_2$–HCl 6,7-*diaminobenzothiazole* (VII) was obtained, m.p. 178° from xylene. (Found: C, 51·2; H, 4·6; N, 25·5. $C_7H_7N_3S$ requires: C, 50·9; H, 4·3; N, 25·4%.)

[1] E. R. Ward and W. H. Poesche, *J. Chem. Soc.* 2825 (1961).

[2] E. R. Ward, W. H. Poesche, D. Higgins and D. D. Heard, *J. Chem. Soc.* 2374 (1962).

[3] E. R. Ward and C. H. Williams, *J. Chem. Soc.* 2248 (1965).

[4] E. R. Ward and D. D. Heard, *J. Chem. Soc.* 4794 (1963).

This new *o*-diamine, treated with 9,10-phenanthraquinone,[5] gave yellow crystals of *dibenzo*-[a.c]*thiazolo*[4,5-*j*]*phenazine*.[6] (Found: C, 74·5; H, 3·3; N, 12·1; S, 9·6. $C_{21}H_{11}N_3S$ requires: C, 74·7; H, 3·3; N, 12·5; S, 9·5%.) The phenazine had no definite m.p. but was soluble in conc. H_2SO_4 to give a characteristic blood-red solution and reprecipitated on dilution.

New heterocyclic ring systems

Preparation of imidazole and triazole ring systems. The procedures adopted were similar to those used by Ward and Heard for 6,7-diamino-1,2,3-benzothiadiazole[4] and Fridman for 2-methyl-6,7-diaminobenzothiazole.[7,8]

A mixture of 6,7-diaminobenzothiazole (0·5 g), 4N HCl (20 ml) and formic acid (1·5 ml) was boiled under reflux for 2 hr. The cooled solution was neutralized with ammonia and the deposited material collected (0·45 g). Recrystallization from water afforded 8H-imidazo[4.5-g]benzothiazole (VIII) as a white solid m.p. 221°. (Found: C, 54·3; H, 2·9; N, 24·2; S, 18·2. $C_8H_5N_3S$ requires: C, 54·8; H, 2·9; N, 24·0; S, 18·3%.)

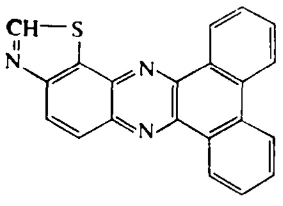
To a solution of 6,7-diaminobenzothiazole (0·5 g) in dil. HCl (10 ml) cooled below 10° was added a conc. $NaNO_2aq$ until excess was present. The solid formed was collected, washed with water and dried to give thiazolo[4.5-g]benzotriazole (IX) as a beige powder (0·43 g) of m.p. 305°. (Found: C, 47·2; H, 2·3; N, 31·6; S, 17·9. $C_7H_4N_4S$ requires: C, 47·7; H, 2·3; N, 31·8; S, 18·2%.)

Preparation of thiadiazole and selenadiazole ring systems. The procedures adopted were similar to those used by Fridman for 2-methyl-6,7-diaminobenzothiazole[9] and Nunn and Ralph for the preparation of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole from *o*-phenylenediamine.[10]

Attempts to bring about condensation of 6,7-diaminobenzothiazole with $SOCl_2$ in benzene (with and without the presence of pyridine) were unsuccessful.

Hot aqueous solutions of SeO_2 (1·0 g in 25 ml) and 6,7-diaminobenzothiazole (0·5 g in 25 ml) were mixed together. After cooling, the deposited solid was collected, washed with water and dried (0·53 g). Recrystallization from glacial AcOH afforded beige plates of thiazolo[4.5-g]-2,1,3-benzoselenadiazole (X) m.p. 216°. (Found: C, 35·1; H, 1·3; N, 17·3; S, 13·6. $C_7H_3N_3SSe$ requires: C, 35·0; H, 1·3; N, 17·5; S, 13·4%.)

[5] F. J. Smith and E. Jones, *A Scheme of Qualitative Organic Analysis* p. 129. Blackie, Glasgow (1962).

[6] 

dibenzo[a,c]thiazolo[4,5-j]phenazine.

[7] S. G. Fridman, *J. Gen. Chem. USSR* **30**, 1534 (1960).

[8] S. G. Fridman, *J. Gen. Chem. USSR* **32**, 1448 (1962).

[9] S. G. Fridman, *J. Gen. Chem. USSR* **31**, 1013 (1961).

[10] A. J. Nunn and J. T. Ralph, *J. Chem. Soc.* 6769 (1965).