RESEARCH ON 2,1,3-THIA- AND SELENADIAZOLE

LIV. Reductive Desulfurization of Benzo-2,1,3-thiadiazoles*

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The stability of the thiadiazole ring in chloro-substituted benzo-2,1,3-thiadiazoles to reductive fission increases with increasing chlorine substitution.

Treatment of benzo-2,1,3-thiadiazole (I) with stannous chloride in HCl leads to the facile fission of the thiadiazole ring with regeneration of o-phenylenediamine [2]. Benzo-2,1,3-thiadiazoles substituted by a methyl group and by chlorine atoms in the benzene ring (e.g., 5-methyl-4-chloro- and 5-methyl-4,7-dichlorobenzo-2,1,3-thiadiazoles) also undergo ready fission under these conditions, the corresponding diamines being formed in high yield [3,4].

Comparative data are given in this paper for this reaction with I and its derivatives bearing either a single methyl group or a single chlorine atom in the benzene ring.

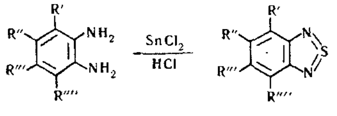
Introduction of a methyl group into the benzene ring does not have an appreciable effect on the course of the reaction, the heterocycle being as easily cleaved as it is in the case of I. The presence in the benzene ring of a chlorine atom, on the other hand, significantly increases the stability of the thiadiazole ring to reduction, and this stability increases further with the introduction of more chlorine atoms into the nucleus, in the series:

Benzothiadiazole	IV	=V	<VII	<IX	=X	<VIII	XI	<XII
Amount (moles) of unreacted benzothiadiazole	—	—	0.001	0.002	0.002	0.004	0.0042	0.0045

The orientation of the chlorine atoms also affects the ring stability.

EXPERIMENTAL

Reduction with stannous chloride in hydrochloric acid. A mixture of 0.005 mole of benzo-2,1,3-thiadiazole (or derivative), 4 g (0.018 mole) of stannous chloride dihydrate, and 30 ml of conc. HCl was boiled for 30 min. The hot mixture was filtered, (unnecessary for compounds I, II, III, IV, V, and VI; benzothiadiazoles I, II, III, and VI dissolved after 2–3 min), and the unreacted benzothiadiazole was washed successively with dilute HCl (d 1.04) and water. The filtrate was evaporated to dryness on a boiling water bath, the residue dissolved in water, basified with 30% caustic soda and extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and the solvent removed. The residue had the melting point described in the literature for the corresponding diamines, and on treatment with a solution of phenanthrenequinone in acetic acid it gave a precipitate giving a coloration with conc H_2SO_4, which was discharged by adding water.



XIII–XXIV I–XII

			Yield (XIII–XXIV)*, g, %
I,	XIII;	R′=R″=R‴=R⁗=H	0.48 (90) [5]
II,	XIV;	R′=CH_3, R″=R‴=R⁗=H	0.49 (80) [5]
III,	XV;	R″=CH_3, R′=R‴=R⁗=H	0.55 (90) [5]
IV,	XVI;	R′=Cl, R″=R‴=R⁗=H	0.57 (80) [6]
V,	XVII;	R″=Cl, R′=R‴=R⁗=H	0.57 (80) [5]
VI,	XVIII;	R″=R‴=CH_3, R′=R⁗=H	0.61 (90)
VII,	XIX;	R″=R‴=Cl, R′=R⁗=H	0.68 (95) [7]
VIII,	XX;	R′=R″=Cl, R‴=R⁗=H	0.16 (90) [8]
IX,	XXI;	R′=R‴=Cl, R″=R⁗=H	0.49 (90) [9,10]
X,	XXII;	R′=R⁗=Cl, R″=R‴=H	0.46 (90) [8]
XI,	XXIII;	R′=R″=R⁗=Cl, R‴=H	0.15 (88) [8]
XII,	XXIV;	R′=R″=R‴=R⁗=Cl	0.11 (89) [8]

*Yields are calculated on reacted benzothiadiazole (I–XII). Constants for the corresponding o-diamines are given in the literature [5–10].

REFERENCES

1. V. G. Pesin, V. A. Sergeev, and E. V. Barkalaya, KhGS [Chemistry of Heterocyclic Compounds], 812, 1968.

2. V. G. Pesin, V. A. Sergeev, and A. M. Khaletskii, ZhOKh, 34, 1263, 1964.

3. V. G. Pesin and R. S. Muravnik, Izv. AN LatvSSR, ser. khim., no. 6, 725, 1964.

4. V. G. Pesin, A. M. Khaletskii, and R. S. Muravnik, USSR patent no. 160506, 160507; Byull. izobr., no. 4, 1964.

5. Chemist's Handbook, Vol. 2 [in Russian], Khimiya, Leningrad-Moscow, 1038, 1964.

6. F. Montanary and R. Passerini, Boll. Sci., facolta chim. ind. Bologna, 11, 42, 1953; C.A., 48, 6436, 1954.

7. G. W. H. Cheesemann, J. Chem. Soc., 1170, 1962.

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*For part LIII, see [1].

8. V. G. Pesin, V. A. Sergeev, and A. M. Khaletskii, ZhOKh, 34, 3028, 1964.
9. R. M. Scott and M. Tomlinson, J. Chem. Soc., 417, 1959.
10. O. N. Witt, Ber., 7, 1604, 1875.

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