*M. Lenič, M. Merslavič, S. Polanc, B. Stanovnik, H. Stavber, D. Struna and M. Tišler*

Department of Chemistry, E. Kardelj University of Ljubljana, 61000 Ljubljana, Yugoslavia

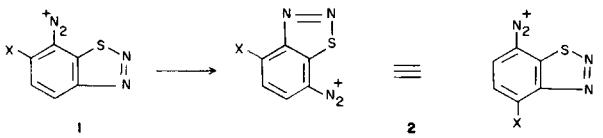
Received February 22, 1980

The preparation of some 6- and /or 7-substituted derivatives of 1,2,3-benzothiadiazole is described. The reactivity of some compounds was investigated in view of the possibility that 1,2,3-benzothiadiazoles may behave as masked diazo compounds. 7-Diazo or diazonium compounds were prepared but no interaction with the thiadiazole part could be observed.

*J. Heterocyclic Chem.*, **17**, 1441 (1980).

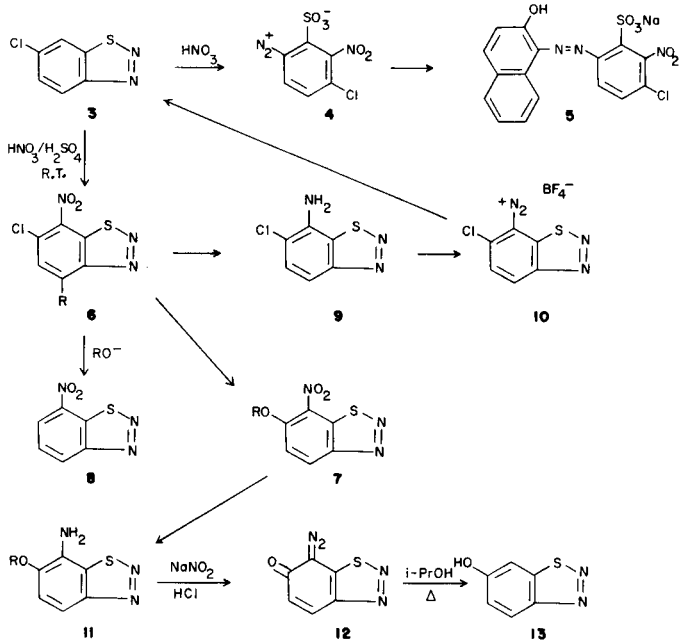
1,2,3-Benzothiadiazoles can be prepared from 1,3,2-benzothiazathiolium salts, obtained from aromatic amines and sulfur monochloride (1). The reported ring opening of the thiadiazole part indicates that 1,2,3-benzothiadiazoles may behave in some respect as masked diazo compounds. This is of particular interest in view of the reported rearrangement of diazonium salts derived from 7-amino-1,2,3-benzothiadiazole. Here, the diazonium group can participate in a new thiadiazole ring formation by simultaneous ring opening of the original thiadiazole part (**1** → **2**) (2). In view of these findings and our previous investigations on heterocyclic diazo compounds (3-9) it seemed of interest to investigate the reactivity of some 6- and/or 7-substituted 1,2,3-benzothiadiazoles.

In a reported synthesis of 7-nitro-1,2,3-benzothiadiazole, concentrated sulfuric acid and potassium nitrate have been used for nitration (2). We have found that by this method 6-chloro-1,2,3-benzothiadiazole (**3**) is converted into the nitro derivative in very small yield. Under more vigorous reaction conditions the thiadiazole ring is cleaved to give 3-chloro-2-nitro-6-diazoniumbenzenesulfonate (**4**) which undergoes coupling to give the azo compound (**5**). Nitration with mixed acid proceeded smoothly at room temperature to give the 7-nitro derivatives (**6**, R = H or methyl) in reasonable yield. The nitro group could not be reduced with titanium trichloride which proved to be an efficient reducing agent for aromatic nitro compounds (10). We found that catalytic reduction over platinum catalyst is a superior method to the stannous chloride reduction method (2).



**1** **2**

As anticipated, the chlorine atom of compound **6** (R = H) could be replaced by methoxy or ethoxy group to give **7** (R = methyl or ethyl). With sodium isopropoxide, however, four compounds were formed as concluded on the basis of tlc examination. With sodium *n*-propoxide



**3** **4** **5** **6** **9** **10** **8** **7** **11** **12** **13**

two products were formed in ratio of 2:1, they were separated by tlc and identified as the 6-*n*-propoxy compound (**7**, R = *n*-propyl) and 7-nitro-1,2,3-benzothiadiazole (**8**).

6-Chloro-1,2,3-benzothiadiazole-7-diazonium tetrafluoroborate (**10**) was obtained from the corresponding amine (**9**). Its stability in dimethyl sulfoxide at various temperatures was monitored in an nmr probe and at moderate temperatures no isomerization (**1** → **2**) could be detected. Even in boiling benzene or toluene the diazonium salt was not changed. However, when the dimethyl sulfoxide solution of the salt (**10**) was treated with hydrazine hydrate at room temperature, nitrogen was immediately evolved and 6-chloro-1,2,3-benzothiadiazole (**3**) was formed. A mechanism, as outlined in Scheme 1 and in accord with our previous findings (4,7) is most probably operating.

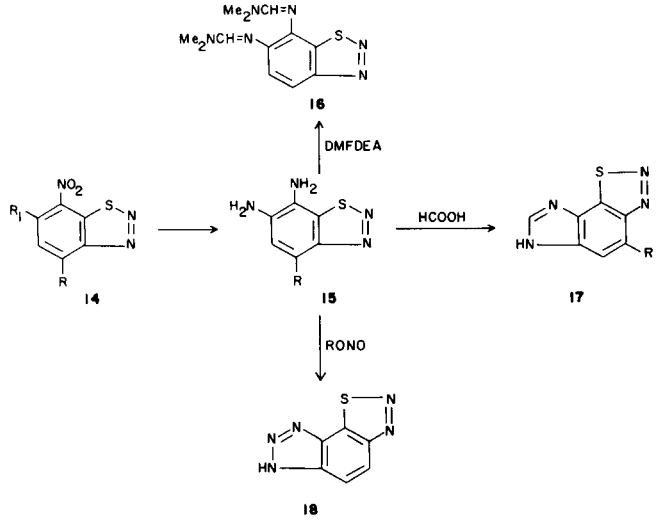
In an attempt to diazotize in the usual manner 6-methoxy- or 6-ethoxy-7-amino-1,2,3-benzothiadiazole **11** (R = methyl or ethyl), 7-diazo-1,2,3-benzothiadiazol-6-one

*0022-152X/80/071441-05$02.25*

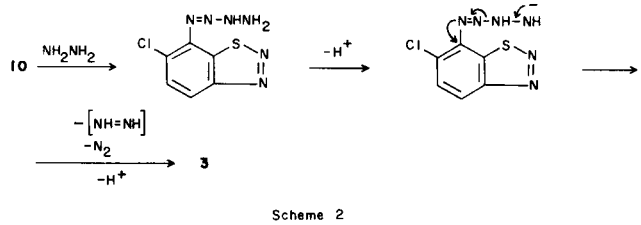
(**12**) was obtained instead in moderate yield. It was necessary to maintain *p*H = 6-7 at the end of the reaction in order to make possible the isolation of the product. The structure of the diazo ketone is in accord with the observed spectroscopic data. The $^1$H nmr spectrum showed two doublets centered at δ 8.35 and 6.76 attributed to the protons at C(4) and C(5) ($J_{4,5}$ = 10 Hz) and a strong absorption band in the ir spectrum at 1600 cm$^{-1}$ (CO). The easy dealkoxylation is undoubtedly due to the presence of hydrochloric acid used in the diazotization procedure, since with isoamyl nitrite in glacial acetic acid, the diazo ketone is not formed. Compound **12** when heated in isopropanol eliminated nitrogen to give the 6-hydroxy derivative (**13**).

The 6,7-diamino compound, **15** (R = H), prepared by reduction of the 6-amino-7-nitro derivative, **14** (R = H, $R_1$ = $NH_2$), was used for the preparation of fused azolo compounds. In an attempt to form a fused imidazole ring with *N*,*N*-dimethylformamide diethyl acetal, which proved to be a good reagent for the formation of imidazole rings from *o*-diamino or similarly functionalized arenes or heterocycles (11,12), only the bis(*N*,*N*-dimethylaminomethylene) derivative (**16**) was obtained. With formic acid, ring closure to **17** was successful and with isoamyl nitrite the corresponding triazole derivative (**18**) was prepared. We were interested in the stability of these tricyclic systems in view of eventual isomerizations (Scheme 2). The thermal stability of the triazolo compound (**18**) was monitored in an nmr probe up to 138° and no structural changes could be observed. In this connection it should be noted that thermal decomposition of 1,2,3-benzothiadiazoles has been observed in several cases (13-17). Similarly, the imidazo analog (**17**) was not changed in dimethyl sulfoxide up to 152° during 1 hour.

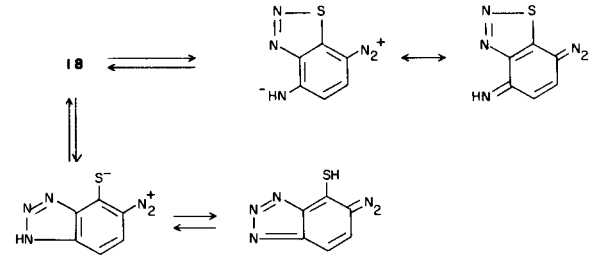
Several similar transformations were performed with the 4-methyl analog. It should be mentioned that the chlorine atom of **14** (R = methyl, $R_1$ = Cl) was easily




Scheme 1




Scheme 2




replaced with hydrazine to give the hydrazino compound, **14** (R = methyl, $R_1$ = $NHNH_2$), and further into the azide (**14**, R = methyl, $R_1$ = $N_3$). However, the attempted reduction of the nitro group of **14** (R = methyl, $R_1$ = $NHNH_2$) afforded the 6,7-diamino compound, **15** (R = methyl).

An interesting feature of these 4-substituted compounds is that the methyl group is coupled with proton at C(7) and/or C(5). $^1$H Nmr spectra of nitro-, bromo- or methoxy-1,2,3-benzothiadiazoles were recorded and interpreted (18), but data for methyl substituted compounds are lacking. We have also observed that in 6-chloro-4-ethyl-1,2,3-benzothiadiazole the methylene group is coupled with protons at C(5) and C(7). It was intended also to prepare the corresponding 7-ethyl and 7-isopropyl derivatives for $^1$H nmr examination, but the reaction with sulfur monochloride yielded no isolable products. Since coupling of methyl group protons to those at positions C(5) and C(7) is seldom observed (19-21) an X-ray structure determination was undertaken in order to confirm the structure of 6-chloro-4-methyl-1,2,3-benzothiadiazole (22). The molecule is essentially planar and shows a normal double bond for N(1)-N(2), partial double bonds for S(1)-N(2) and S(1)-C(7a) and a considerable π-system conjugation in the benzene part of the molecule.

## EXPERIMENTAL

Melting points were determined on a hot-stage microscope and are uncorrected. $^1$H Nmr spectra were recorded on a JEOL JNM C60-HL spectrometer. Chemical shifts are given in ppm downfield from TMS. Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6L instrument.

The following 1,2,3-benzothiadiazoles were prepared according to the methods described in the literature: 6-chloro, m.p. 77° (lit. (1) m.p. 77°); nmr (deuteriochloroform): δ 8.63 (d, $H_4$),

7.63 (dd, $H_5$), 8.15 (d, $H_7$), $J_{4,5}$ = 9.0, $J_{5,7}$ = 2.0 Hz; 6-methoxy-7-nitro-, m.p. 158-160° (lit. (2) m.p. 161-162°); nmr (DMSO-$d_6$): δ 9.16 (d, $H_4$), 7.95 (d, $H_5$), 4.30 (s, OMe), $J_{4,5}$ = 9.0 Hz; 7-amino-6-methoxy-, m.p. 105-106° (lit. (2) m.p. 102-103°); nmr (DMSO-$d_6$): δ 7.95 (d, $H_4$), 7.40 (d, $H_5$), 3.96 (s, OMe), $J_{4,5}$ = 9.0 Hz; 6,7-diamino-, m.p. 195° (lit. (23) m.p. 195°); and 6-chloro-4-methyl-1,2,3-benzothiadiazole, m.p. 62° (lit. (1) m.p. 63.5-64.5°), nmr (deuteriochloroform): δ 7.87 (m, $H_7$), 7.35 (m, $H_5$), 3.03 (dd, Me), $J_{5,7}$ = 2.4, $J_{H_5,Me}$ = 0.8, $J_{H_7,Me}$ = 0.6 Hz.

3-Chloro-6-diazo-2-nitrobenzenesulfonate (**4**).

To ice-cold concentrated sulfuric acid (12 ml.) concentrated nitric acid (5 ml.) was added slowly under stirring. Thereafter, 6-chloro-1,2,3-benzothiadiazole (2.5 g.) was added portionwise with stirring. The reaction mixture was heated at 70° for 3 hours. Upon cooling, the reaction mixture was poured on ice (120 g.) and the precipitate was filtered and washed thoroughly with water and ethanol (1.6 g., 44%), m.p. 165-168°; nmr (DMSO-$d_6$): δ 8.47 (d, $H_4$), 9.03 (d, $H_5$), $J_{4,5}$ = 9 Hz.

*Anal.* Calcd. for $C_6H_2ClN_3O_5S$: C, 27.33; H, 0.75; N, 15.94. Found: C, 27.42; H, 1.28; N, 16.32.

The diazo compound was dissolved in ethanol and an ethanolic solution of 2-naphthol was added. After addition of the calculated amount of sodium hydroxide the sodium salt of the coupling product (**5**) separated and was filtered (yield 38%), m.p. > 290° (from ethanol).

*Anal.* Calcd. for $C_{16}H_9ClN_3O_6S{\cdot}Na$: C, 44.68; H, 2.11; N, 9.77. Found: C, 44.68; H, 2.47; N, 9.90.

6-Chloro-7-nitro-1,2,3-benzothiadiazole (**6**, R = H).

To stirred ice-cold concentrated sulfuric acid (12 ml.) concentrated nitric acid (5 ml.) was added slowly. Under stirring 6-chloro-1,2,3-benzothiadiazole (2.5 g.) was added portionwise. The reaction mixture was left at room temperature for 6 hours and then poured on crushed ice (120 g.). After standing for some time, the product was filtered, dried and crystallized from chloroform and petroleum ether (1.9 g., 60%), m.p. 97-99° (lit. (2) m.p. 99-101°); nmr (DMSO-$d_6$): δ 9.10 (d, $H_4$), 8.13 (d, $H_5$), $J_{4,5}$ = 9 Hz.

*Anal.* Calcd. for $C_6H_2ClN_3O_2S$: C, 33.42; H, 0.93; N, 19.49. Found: C, 33.70; H, 1.10; N, 19.59.

6-Chloro-4-methyl-7-nitro-1,2,3-benzothiadiazole (**6**, R = Me).

This compound was obtained in a similar manner in 53% yield, m.p. 155-163° (lit. (2) m.p. 160°).

6-Chloro-7-amino-1,2,3-benzothiadiazole (**9**).

A mixture of 6-chloro-7-nitro-1,2,3-benzothiadiazole (**6**, R = H) (0.5 g.), ethanol (50 ml.) and platinum catalyst (0.1 g. of 5% on charcoal) was shaken in an atmosphere of hydrogen (2 atmospheres) in an autoclave for 20 hours. Upon filtration the solvent was evaporated and the residue purified by sublimation (0.394 g., 91%), m.p. 155-156° (lit. (2) m.p. 157°); nmr (DMSO-$d_6$): δ 7.98 (d, $H_4$), 7.66 (d, $H_5$), $J_{4,5}$ = 9 Hz.

6-Chloro-1,2,3-benzothiadiazole-7-diazonium Tetrafluoroborate (**10**).

7-Amino-6-chloro-1,2,3-benzothiadiazole (0.2 g.) was added to concentrated hydrochloric acid (2 ml.) under stirring. The solution was cooled to 0° and aqueous solution of sodium nitrite (0.09 g. in 5 ml. water) was added dropwise. After stirring for 20 minutes at 0°, tetrafluoroboric acid (4 ml. of 50%) was added. The reaction mixture was stirred for 5 minutes and left in dark at room temperature for 12 hours. The precipitate was filtered, methanol (15 ml.) was added and the mixture stirred at room temperature for 15 minutes. The product was filtered and washed with methanol (5 ml.). The filtrate was evaporated to about 1/5 of its original volume and ether (20 ml.) was added. The product was filtered and washed with ether, (0.04 g., 13%), m.p. 165-170° dec.; nmr (DMSO-$d_6$): δ 8.50 (d, $H_4$), 6.50 (d, $H_5$), $J_{4,5}$ = 9.5 Hz.

*Anal.* Calcd. for $C_6H_2ClN_4S{\cdot}BF_4$: C, 25.34; H, 0.71; N, 19.70. Found: C, 26.99; H, 0.79; N, 18.69.

Repeated attempts to obtain an analytically pure sample of **10** were unsuccessful.

The diazonium salt, when dissolved in dimethyl sulfoxide and treated with hydrazine hydrate was transformed into 6-chloro-1,2,3-benzothiadiazole (**3**).

6-Ethoxy-7-nitro-1,2,3-benzothiadiazole (**7**, R = Et).

An ethanolic solution of sodium ethoxide was prepared from sodium (0.046 g.) and ethanol (8.5 ml.). To this solution the 6-chloro compound (**6**, R = H) (0.431 g.) was added and the reaction mixture was heated under reflux for 30 minutes. The solvent was evaporated *in vacuo*, the residue was treated with water (5 ml.) and filtered, m.p. 112-115° (from ethanol and water) (0.315 g., 70%); ms: $M^+$ = 225; nmr (DMSO-$d_6$): δ 9.0 (d, $H_4$), 7.81 (d, $H_5$), 4.50 (q, $CH_2Me$), 1.49 (t, $CH_2CH_3$), $J_{4,5}$ = 9.5, $J_{Et}$ = 7.0 Hz.

*Anal.* Calcd. for $C_8H_7N_3O_3S$: C, 42.67; H, 3.13; N, 18.65. Found: C, 42.44; H, 3.00; N, 18.77.

7-Amino-6-ethoxy-1,2,3-benzothiadiazole (**11**, R = Et).

The above nitro compound (**7**, R = Et) (0.4 g.) was added to a solution of stannous chloride monohydrate (2.0 g.) in concentrated hydrochloric acid (4 ml.). The reaction mixture was heated under reflux for 5 minutes, cooled to room temperature and diluted with water (6 ml.). Under stirring the reaction mixture was added slowly to a solution of aqueous sodium hydroxide (10 ml. of 30%). The aqueous solution was extracted with chloroform (four times with 20 ml.), the combined extracts were dried over anhydrous sodium sulfate, charcoaled, filtered and the solvent was evaporated to dryness. The residual oil was distilled *in vacuo* at 130°/1 mm (0.2 g., 58%); ms: $M^+$ = 195; nmr (deuteriochloroform): δ 7.98 (d, $H_4$), 7.17 (d, $H_5$), $J_{4,5}$ = 9 Hz.

*Anal.* Calcd. for $C_8H_9N_3OS$: C, 49.23; H, 4.64. Found: C, 49,50; H, 4.69.

Reaction of 6-Chloro-7-nitro-1,2,3-benzothiadiazole with Sodium *n*-Propoxide.

A solution of sodium *n*-propoxide was prepared from sodium (0.046 g.) and dry and freshly distilled 1-propanol (9 ml.). To this solution 6-chloro-7-nitro-1,2,3-benzothiadiazole (0.431 g.) was added and the reaction mixture was heated under reflux for 1 hour. The solvent was evaporated and the semisolid residue was dissolved in methanol (5 ml.). On hand of tlc the presence of two compounds was established and they were separated on plates (Merck DC-Fertigplatten Kieselgel 60 F 254, 2 mm, solvent mixture chloroform and petroleum ether, 1:1; elution with methanol). The process was repeated three times and from 0.8 g. of crude product there were obtained 7-nitro-1,2,3-benzothiadiazole (0.4 g., 50%) and its 6-*n*-propoxy derivative (0.2 g., 25%).

6-*n*-Propoxy-7-nitro-1,2,3-benzothiadiazole (**7**, R = *n*-Pr).

This compound had m.p. 77-78° (from ethanol and water); ms: $M^+$ = 239; nmr (deuteriochloroform): δ 8.89 (d, $H_4$), 7.56 (d, $H_5$), $J_{4,5}$ = 9.7 Hz.

*Anal.* Calcd. for $C_9H_9N_3O_3S$: C, 45.00; H, 3.77. Found:

C, 45.47; H, 3.38.

7-Nitro-1,2,3-benzothiadiazole (**8**).

This compound had m.p. 74-76° (lit. (24) m.p. 106°) (from ethanol and water); ms: $M^+$ = 181; nmr (deuteriochloroform): δ 9.10 and 8.79 (dd, $H_4$ and $H_6$), 7.96 (t, $H_5$), $J_{4,5} = J_{5,6}$ = 8.0 Hz, $J_{4,6}$ = 1.3 Hz.

*Anal.* Calcd. for $C_6H_3N_3O_2S$: C, 39.79; H, 1.67. Found: C, 40.21; H, 1.88.

7-Diazo-1,2,3-benzothiadiazol-6-one (**12**).

6-Ethoxy-7-amino-1,2,3-benzothiadiazole (**11**, R = Et) (0.4 g.) was dissolved in concentrated hydrochloric acid (13.7 ml.) under stirring. The cooled solution (0-5°) was treated dropwise with aqueous solution of sodium nitrite (0.17 g. in 2 ml.). The reaction mixture was stirred for 10 minutes and aqueous tetrafluoroboric acid (9.8 ml. of 50%) was added. The reaction mixture was neutralized with saturated aqueous sodium bicarbonate to *p*H 6-7, left at room temperature for 30 minutes and the brown precipitate was filtered. The filtrate was extracted with chloroform (4 times with 20 ml.), the combined extracts were dried over anhydrous sodium sulfate, the filtrate was treated with a small amount of charcoal and left at room temperature for 2 hours. Upon filtration the solvent was evaporated and the product was dissolved in chloroform and precipitated with petroleum ether, m.p. 91-93° dec (0.19 g., 52%); ms: $M^+$ = 178; nmr (deuteriochloroform): δ 8.35 (d, $H_4$), 6.76 (d, $H_5$), $J_{4,5}$ = 10 Hz.

The same compound could be prepared in 12.5% yield from 6-methoxy-7-amino-1,2,3-benzothiadiazole (**11**, R = Me) by the above procedure. It decomposes easily and was used immediately for further transformations.

Formation of 6-Hydroxy-1,2,3-benzothiadiazole (**13**) from 7-Diazo-1,2,3-benzothiadiazol-6-one.

A solution of the 7-diazo compound (**12**) (0.15 g.) in isopropyl alcohol (15 ml.) was heated under reflux for 6 hours. The solvent was evaporated *in vacuo* and the residue was purified by sublimation *in vacuo* and crystallization from methanol and water (yield 0.104 g., 81%), m.p. 191° (lit. (24) gives m.p. 219°, lit. (25) gives m.p. 211°); ms: $M^+$ = 152; nmr (methanol-$d_4$): δ 8.58 (dd, $H_7$), 7.61 (dd, $H_4$), 7.31 (dd, $H_5$), $J_{4,5}$ = 9.0, $J_{5,7}$ = 2.6, $J_{4,7}$ = 0.5 Hz.

The same compound could be prepared from the diazo compound when heated in ethanol (yield 78%).

6-Amino-7-nitro-1,2,3-benzothiadiazole (**14**, R = H, $R_1 = NH_2$).

The 6-chloro-7-nitro compound (**6**, R = H) (0.8 g.) and concentrated aqueous ammonia (20 ml.) were heated under reflux for 2 hours. Upon cooling, the product was filtered and washed with water (15 ml.) (0.54 g., 74%), m.p. 310° dec. (from acetic acid) (lit. (23) m.p. 310°). The compound was used for the synthesis of 6,7-diamino-1,2,3-benzothiadiazole (**15**, R = H) (23).

Reaction of 6,7-Diamino-1,2,3-benzothiadiazole with *N,N*-Dimethylformamide Diethyl Acetal.

A mixture of the diamino compound (**15**, R = H) (0.30 g.) and *N,N*-dimethylformamide diethyl acetal (1,5 ml.) was heated under reflux for 2 hours. Excess of the reagent was removed *in vacuo* and the residue was treated with chloroform (6 ml.) and the reaction mixture stirred at room temperature for 1 hour. Upon filtration charcoal was added, the mixture was heated to boil and then left to stand at room temperature overnight. The filtrate was evaporated to dryness, benzene (2 ml.) was added and under stirring *n*-hexane (14 ml.) was added. The mixture was left in a refrigerator overnight, the product was filtered and washed with *n*-hexane. Compound **16** was obtained in 20% yield (0.1 g.), m.p. 86-88°; ms: $M^+$ = 276; nmr (DMSO-$d_6$): δ 7.94 (d, $H_4$), 7.21 (d, $H_5$), 8.61 and 7.87 (s, 6-N=CH- and 7-N=CH-), 2.97 (s, $NMe_2$), $J_{4,5}$ = 8.7 Hz.

*Anal.* Calcd. for $C_{12}H_{16}N_6S$: C, 52.15; H, 5.84; N, 30.41. Found: C, 52.25; H, 5.81; N, 30.41.

However, when the diamino compound (**15**, R = H) (0.144 g.) and formic acid (4 ml. of 85%) were heated under reflux, imidazo[4,5-*g*]-1,2,3-benzothiadiazole (**17**, R = H) was obtained (0.106 g., 67%), m.p. 228-230° (lit. (23) m.p. 230° dec.); ms: $M^+$ = 176; nmr (DMSO-$d_6$): δ 8.59 and 8.0 (d, $H_4$ and $H_5$), 8.61 (s, $H_7$), $J_{4,5}$ = 9.5 Hz.

*Anal.* Calcd. for $C_7H_4N_4S$: C, 47.66; H, 2.28. Found: C, 47.30; H, 2.45.

Upon treatment of a solution of the diamino compound (**15**, R = H) in acetic acid with isoamyl nitrite the corresponding triazolo[4,5-*g*]-1,2,3-benzothiadiazole (**18**) was obtained (53% yield), m.p. 229-233° (upon sublimation), lit. (23) gives m.p. 236°; ms: $M^+$ = 177; nmr (DMSO-$d_6$): δ 8.73 and 8.15 (d, $H_4$ and $H_5$), $J_{4,5}$ = 9.5 Hz.

6-Hydrazino-4-methyl-7-nitro-1,2,3-benzothiadiazole (**14**, R = Me, $R_1 = NHNH_2$).

A suspension of the corresponding chloro compound (**14**, R = Me, $R_1$ = Cl) (1.15 g.) in ethanol (20 ml.) was treated with ethanolic hydrazine hydrate (1 g. of 80% in 10 ml.) and the mixture was heated under reflux for 2 hours. The solvent was evaporated and the residue was suspended in water (5 ml.). The product was filtered, washed with water (10 ml.) and dried (0.7 g., 62%), m.p. 215-217° (from ethanol and water); ms: $M^+$ = 225; nmr (methanol-$d_4$): δ 7.72 (q, $H_5$), 2.87 (d, Me), $J_{H_5Me}$ = 1.1 Hz.

*Anal.* Calcd. for $C_7H_7N_5O_2S$: C, 37.32; H, 3.13; N, 31.10. Found: C, 37.12; H, 3.08; N, 31.02.

The compound formed a benzylidene derivative, m.p. 265-267°, an ethylidene derivative, m.p. 190-193°, an isopropylidene derivative, m.p. 240° dec.

6,7-Diamino-4-methyl-1,2,3-benzothiadiazole (**15**, R = Me).

The above hydrazino compound (**14**, R = Me, $R_1 = NHNH_2$) (0.225 g.) was treated with a solution of stannous chloride dihydrate (1.12 g.) in concentrated hydrochloric acid (2 ml.) and the reaction mixture was heated under reflux for 5 minutes. Upon cooling and dilution with water (3 ml.) aqueous sodium hydroxide (5 g. of 30%) was added dropwise. The reaction mixture was stirred at room temperature for 30 minutes, the product was filtered, washed with water (7 ml.) and dried. It was crystallized from chloroform and petroleum ether (0.110 g., 61%), m.p. 201-205°. The compound had ms: $M^+$ = 180; nmr (DMSO-$d_6$): δ 6.78 (q, $H_5$), 2.70 (d, Me).

*Anal.* Calcd. for $C_7H_8N_4S$: C, 46.65; H, 4.47; N, 31.09. Found: C, 46.40; H, 4.53; N, 30.99.

4-Methylimidazo[4,5-*g*]-1,2,3-benzothiadiazole (**17**, R = Me).

A mixture of the above diamino compound (**15**, R = Me) (0.15 g.) and formic acid (5 ml. of 85%) was heated under reflux for 2 hours. Upon evaporation to dryness the residue was crystallized from water (0.06 g., 38%), m.p. 240° dec.; ms: $M^+$ = 190; nmr (methanol-$d_4$): δ 8.36 (s, $H_7$), 7.59 (q, $H_5$), 3.03 (d, Me), $J_{H_5Me}$ = 1.0 Hz.

*Anal.* Calcd. for $C_8H_6N_4S$: C, 50.51; H, 3.18; N, 29.45. Found: C, 50.44; H, 3.22; N, 29.60.

Acknowledgment.

We wish to acknowledge financial support of this work by a grant from the Research Community of Slovenia.

## REFERENCES AND NOTES

(1) P. Kirby, S. B. Soloway, J. H. Davies and S. B. Webb, *J. Chem. Soc. C*, 2250 (1970).

(2) E. Haddock, P. Kirby and A. W. Johnson, *ibid.*, 2514 (1970).

(3) B. Stanovnik, M. Tišler, B. Kirn and I. Kovač, *J. Heterocyclic Chem.*, **16**, 195 (1979).

(4) M. Kočevar, B. Stanovnik and M. Tišler, *ibid.*, **15**, 1175 (1978).

(5) B. Stanovnik, M. Tišler, J. Bradač, B. Budič, B. Koren and B. Mozetič-Reščič, *Heterocycles*, **12**, 457 (1979).

(6) M. Tišler, B. Stanovnik and Z. Zrimšek, *Vestn. Slov. Kem. Drus.*, **26**, 163 (1979).

(7) L. Dežman, D. Janežič, M. Kokalj, E. Kozak, J. Primc, B. Stanovnik, M. Tišler and O. Zaplotnik-Naglič, *Tetrahedron*, **33**, 2851 (1977).

(8) S. Gorjan, B. Klemenc, M. Starič, B. Stanovnik and M. Tišler, *Monatsh. Chem.*, **107**, 1199 (1976).

(9) M. Kočevar, D. Kolman, H. Krajnc, S. Polanc, B. Porovne, B. Stanovnik and M. Tišler, *Tetrahedron*, **32**, 725 (1976).

(10) T. L. Ho and C. M. Wong, *Synthesis*, 45 (1974).

(11) B. Stanovnik and M. Tišler, *ibid.*, 120 (1974).

(12) M. Debeljak-Šuštar, B. Stanovnik, M. Tišler and Z. Zrimšek, *J. Org. Chem.*, **43**, 393 (1978).

(13) P. Jacobson and H. Janssen, *Ann. Chem.*, **277**, 209 (1893).

(14) G. Seybold and C. Heibl, *Angew. Chem.*, **87**, 171 (1975).

(15) L. Benati, P. C. Montevecchi and G. Zanardi, *J. Org. Chem.*, **42**, 575 (1977).

(16) R. Huisgen and V. Werberndorfer, *Experientia*, **14**, 566 (1961).

(17) R. C. White, J. Scoby and T. D. Roberts, *Tetrahedron Letters*, 2785 (1979).

(18) W. H. Poesche, *J. Chem. Soc. B*, 368 (1971).

(19) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2704 (1963).

(20) M. Barfield and B. Chakrabarti, *ibid.*, **91**, 4346 (1969).

(21) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(22) L. Golič, I. Leban, B. Stanovnik and M. Tišler, *Acta Crystallogr.*, **B35**, 3114 (1979).

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

(24) E. R. Ward, W. H. Poesche, D. Higgins and D. D. Heard, *ibid.*, 2374 (1962).

(25) K. Fries, M. Vorbrodt, and G. Siebert, *Ann. Chem.*, **454**, 172 (1927).