Novel Pyrrole-Annulated Heterocyclic Systems. Synthesis of 10*H*-Pyrrolo[1,2-*b*][1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-Dioxide

Roberto Di Santo, Roberta Costi and Marino Artico*

Dipartimento di Studi Farmaceutici, Università di Roma "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy

Silvio Massa

Dipartimento Farmaco Chimico Tecnologico, Università degli Studi di Siena, Banchi di Sotto 55, I-53100 Siena, Italy

Received April 1, 1996

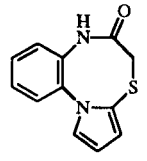
Intramolecular cyclization of 1-(2-aminophenylsulfonyl)-1*H*-pyrrole-2-acetic acid **5** gave 10*H*-pyrrolo[1,2-*b*][1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-dioxide **4**, a novel heterocyclic system of pyrrolobenzothiadiazocine family. Compound **5** was obtained starting from 2-nitrobenzenesulfonyl chloride with ethyl 1*H*-pyrrole-2-(α-oxo)acetate, which were condensed to afford 1-(2-nitrophenylsulfonyl)-1*H*-pyrrole-2-(α-oxo)acetate **13**. Reduction of **13** gave the amino ester **7**, which was hydrolyzed to the required aminoacid **5**. The synthesis of 7-chloro-10*H*-pyrrolo[1,2-*b*][1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-dioxide **16** is also described.

J. Heterocyclic Chem., **33**, 2019 (1996).

Differently from pyrrolobenzothiadiazepine systems, which have been widely investigated [1-7], synthetic studies of benzothiadiazocine rings annulated with pyrrole have received little attention.

Cheeseman some years ago reported on the synthesis of pyrrolo[1,2-*a*][3,1,6]benzothiadiazocine derivatives **1** [8,9] and recently we described the synthetic routes leading to 9*H*-pyrrolo[2,1-*b*][1,3,6]benzothiadiazocin-10(11*H*)-one (**2**) [10] and 10*H*-pyrrolo[1,2-*b*][1,2,5]benzothiadiazocine 5,5-dioxide (**3**) [11], two 6,8,5-membered tricyclic systems useful for the design of new potential anti-HIV agents [12].

As a part of our continuing efforts in the chemistry of pyrrole annulated heterocyclic systems we have devised a synthesis for 10*H*-pyrrolo[1,2-*b*] [1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-dioxide (**4**), which is isomeric with **3**.



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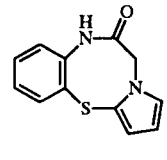

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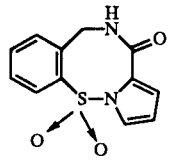

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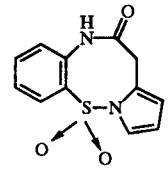

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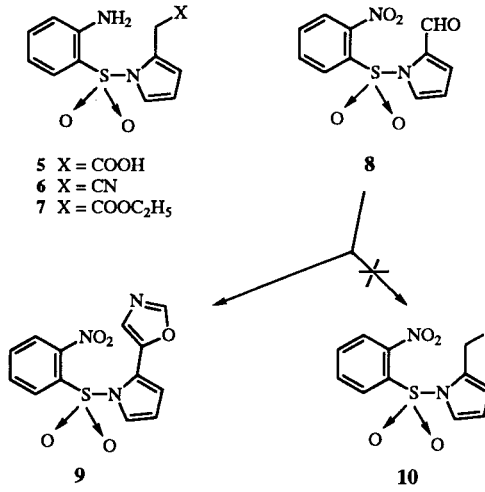
As a likely route to obtain derivative **4** we chose the intramolecular cyclization of 1-(2-aminophenylsulfonyl)-1*H*-pyrrole-2-acetic acid (**5**), which can be obtained by hydrolysis of the corresponding nitrile **6** or ethyl ester **7**.

Scheme 1



5 X = COOH
6 X = CN
7 X = $COOC_2H_5$

8

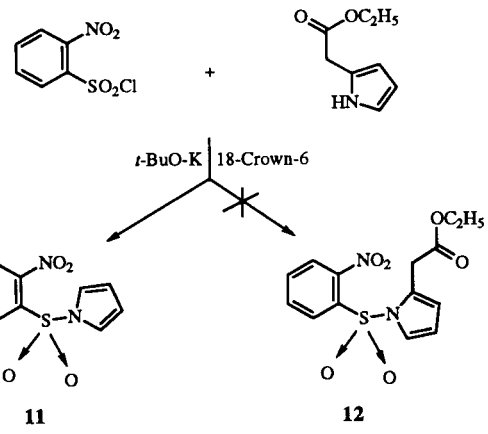
9

10

Attempts to obtain **6** starting from 1-(2-nitrophenylsulfonyl)-1*H*-pyrrole-2-carboxaldehyde (**8**) [2] were unsuccessful. In fact, contrary to all expectation, the reaction of **8** with toluene-4-sulfonyl methyl isocyanide under literature conditions [13,14] afforded 1-(2-nitrophenylsulfonyl)-2-(5-oxazolyl)-1*H*-pyrrole (**9**) (Scheme 1) instead of the expected nitrile **10**, neither was such a derivative produced by the reaction between aldehyde **8** and cyanophosphates followed by treatment with samarium diiodide [15].

We then tried to prepare the nitroester **12** by condensation of 2-nitrobenzenesulfonyl chloride with ethyl 1*H*-pyrrole-2-acetate, but the acetate moiety functioned as a leaving group during the reaction with formation of 1-(2-nitrophenylsulfonyl)-1*H*-pyrrole (**11**) [2] as the sole product (Scheme 2). Also the reaction between 1-(2-nitrophenylsulfonyl)-1*H*-pyrrole (**11**) and ethyl iodoacetate

Scheme 2



11 12

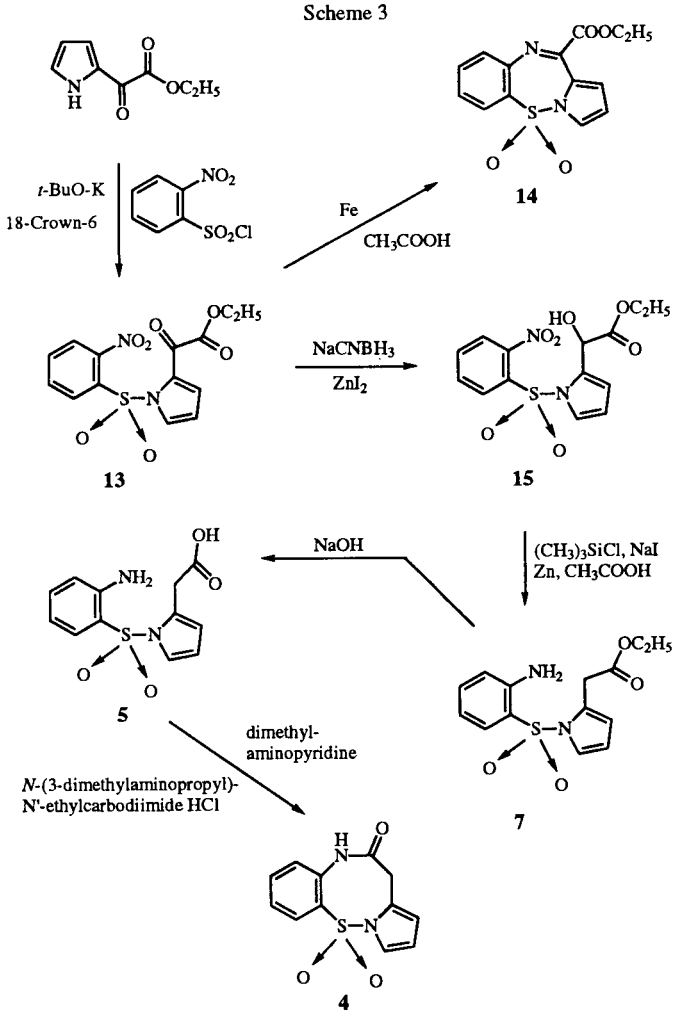
according to Baciocchi [16] did not produce the required pyrroleacetate **12**. Finally, we were able to prepare the ester **7** as depicted in Scheme 3.

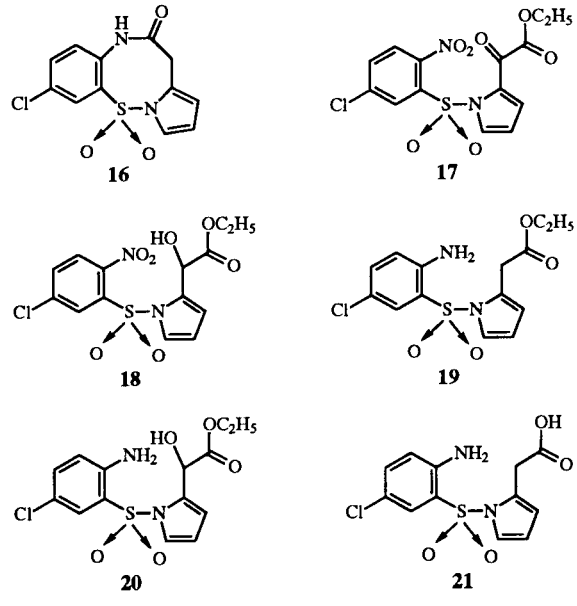
The synthesis of **7** started from ethyl 1-(2-nitrophenylsulfonyl)-1*H*-pyrrole-2-(α-oxo)acetate (**13**), which was prepared by reacting ethyl 1*H*-pyrrole-2-(α-oxo)acetate [17] with 2-nitrobenzenesulfonyl chloride. The one-step reduction of the ketone function to a methylene group with a lithium aluminum hydride-aluminum trichloride mixture [18] failed. Likewise, the procedure based on the reaction of the ketoester **13** with sodium borohydride in trifluoroacetic acid was unproductive [19]. The reduction of the nitroglyoxylic ester **13** with iron powder in acetic acid led to pyrrolobenzothiadiazepine derivative **14**. Lastly, we obtained **7** by a two-step pathway based on the reaction of nitro-ester **13** with sodium cyanoborohydride and zinc iodide [20] with formation of the nitro-alcohol **15**, followed by a one-pot conversion of the latter derivative into the required amino ester **7** using as reducing reagent the chlorotrimethylsilane-sodium iodide-zinc system [21].

Alkaline hydrolysis of ethyl 1-(2-aminophenylsulfonyl)-1*H*-pyrrole-2-acetate (**7**) afforded the corresponding acid **5**, which was then cyclized to the title compound **4** by treatment with *N*-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride-dimethylaminopyridine system (Scheme 3).

The procedure depicted in Scheme 3 was also adopted for the synthesis of 7-chloro-10*H*-pyrrolo[1,2-*b*]-[1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-dioxide (**16**). The glyoxylate **17** formed easily using potassium *tert*-butoxide and 18-crown-6 as a condensing system in the reaction between 5-chloro-2-nitrobenzenesulfonyl chloride and ethyl 1*H*-pyrrole-2-(α-oxo)acetate. Moreover, the formation of the ethyl 1-(2-amino-5-chlorophenylsulfonyl)-1*H*-pyrrole-2-acetate (**19**) *via* the nitro-alcohol **18** was affected by the presence of ethyl 1-(2-amino-5-chlorophenylsulfonyl)-1*H*-pyrrole-2-(α-hydroxy)acetic acid (**20**) as a side-product. As above reported hydrolysis of **19** to the acid **21** followed by ring closure of the latter derivative with *N*-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride-dimethylaminopyridine gave **16**.

Scheme 3





EXPERIMENTAL

Melting points were determined on an Electrothermal IA6304 apparatus and are uncorrected. Infrared spectra (nujol mulls) were run on a Perkin Elmer 1310 spectrophotometer. The ^{1}H-nmr spectra were recorded with either a Bruker AC 200 or a Varian Gemini 200 (200 MHz) using TMS as the internal standard. Column chromatography purifications were performed on silica gel Merck (70-230 Mesh) and alumina Merck (70-230 Mesh). Stratocrom SIF Carlo Erba (silica gel precoated plates with fluorescent indicator) and Stratocrom ALF Carlo Erba (aluminium oxide precoated plates with fluorescent indicator) were employed for tlc. Elemental analyses were performed by M. Zancato, Padova, Italy. Organic extracts were dried over anhydrous sodium sulfate. Evaporation of solvents after reactions and extractions involved the use of a rotatory evaporator (Büchi) operating at reduced pressure (approximately 20 bar).

Ethyl 1-(2-Nitrophenylsulfonyl)-1*H*-pyrrole-2-(α-oxo)acetate (**13**).

A solution of ethyl 1*H*-pyrrole-2-(α-oxo)acetate (7.4 g, 0.044 mole) in anhydrous tetrahydrofuran (90 ml) was added into a well stirred suspension of 18-crown-6 and potassium *tert*-butoxide (5.6 g, 0.052 mole) in the same solvent (90 ml). The mixture was stirred at room temperature for 15 minutes and cooled at 0°, then a solution of 2-nitrobenzenesulfonyl chloride (13.7 g, 0.062 mole) in anhydrous tetrahydrofuran (90 ml) was added dropwise. After the addition, the solution was stirred at room temperature for 2 hours then diluted with water (250 ml), concentrated and treated with ethyl acetate (250 ml). The organic solution was washed with brine (3 x 200 ml), dried and the solvent was evaporated to give the crude product, which was chromatographed on a silica gel column (diethyl ether/*n*-hexane 1:1 as the eluent) to give pure **13** (6.7 g, 43% yield), mp 130-131° (from benzene); ir: 1720 cm^{-1} (C=O ester) and 1660 (C=O ketone); pmr (deuteriochloroform): δ 1.37 (t, 3H, CH_3), 4.36 (q, 2H, CH_2), 6.49 (m, 1H, pyrrole C_4-H), 7.61 (m, 1H, pyrrole C_3-H), 7.75-7.81 (m, 3H, benzene H), 7.83 (m, 1H, pyrrole C_5-H) and 8.61 (m, 1H, benzene C_6-H).

Anal. Calcd. for $C_{14}H_{12}N_2O_7S$: C, 47.73; H, 3.43; N, 7.95; S, 9.10. Found: C, 47.58; H, 3.28; N, 7.84; S, 9.01.

Ethyl 1-(5-Chloro-2-nitrophenylsulfonyl)-1*H*-pyrrole-2-(α-oxo)acetate (**17**).

Compound **17** was prepared as reported for derivative **13** from 5-chloro-2-nitrobenzenesulfonyl chloride and ethyl 1*H*-pyrrole-2-(α-oxo)acetate. Compound **17** was obtained in 83% yield, mp 127-128° (from benzene/cyclohexane); ir: 1725 cm^{-1} (C=O ester) and 1660 (C=O ketone); pmr (deuteriochloroform): δ 1.36 (t, 3H, CH_3), 4.35 (q, 2H, CH_2), 6.48 (m, 1H, pyrrole C_4-H), 7.59 (m, 1H, pyrrole C_3-H), 7.72-7.80 (m, 2H, benzene C_3-H and C_4-H), 7.86 (m, 1H, pyrrole C_5-H) and 8.50 (d, 1H, J_m = 2.0 Hz, benzene C_6-H).

Anal. Calcd. for $C_{14}H_{11}ClN_2O_7S$: C, 43.48; H, 2.87; N, 7.24; Cl, 9.17; S, 8.29. Found: C, 43.54; H, 2.98; N, 7.46; Cl, 9.10; S, 8.34.

Ethyl 1-(2-Nitrophenylsulfonyl)-1*H*-pyrrole-2-(α-hydroxy)-acetate (**15**).

Zinc iodide (700 mg, 0.002 mole) and sodium cyanoborohydride (690 mg, 0.011 mole) were added to a solution of **13** (530 mg, 0.0015 mole) in 1,2-dichloroethane (8 ml) and the suspension was stirred at room temperature for 15 hours. After this time the mixture was filtered on celite. The organic solution was dried and the solvent evaporated to give pure **15**, 460 mg (87% yield), mp 88-90° (from benzene/cyclohexane), ir: 3440 cm^{-1} (OH) and 1730 (C=O); pmr (deuteriochloroform): δ 1.22 (t, 3H, CH_3), 3.30 (s, broad, 1H, OH), 4.21 (q, 2H, CH_2), 5.47 (s, 1H, CH), 6.32 (m, 2H, pyrrole β-H), 7.27-7.81 (m, 5H, pyrrole α-H and benzene H).

Anal. Calcd. for $C_{14}H_{14}N_2O_7S$: C, 47.46; H, 3.98; N, 7.91; S, 9.05. Found: C, 47.51; H, 3.98; N, 7.88; S, 9.05.

Ethyl 1-(5-Chloro-2-nitrophenylsulfonyl)-1*H*-pyrrole-2-(α-hydroxy)acetate (**18**).

Prepared as reported above, **18** was purified by chromatography on silica gel column (chloroform as eluent), 94% yield, mp 105-107° (from benzene/*n*-hexane); ir: 3420 cm^{-1} (OH) and 1735 (C=O); pmr (deuteriochloroform): δ 1.27 (t, 3H, CH_3), 3.21 (d, 1H, J = 5.4 Hz, OH), 4.27 (q, 2H, CH_2), 5.49 (d, 1H, J = 5.4 Hz, CH), 6.37 (m, 2H, pyrrole β-H), 7.26-7.37 (m, 2H, pyrrole α-H and benzene C_6-H), 7.65 (dd, 1H, J_o = 8.6 Hz, J_m = 2.0 Hz, benzene C_4-H), 7.82 (d, 1H, J_o = 8.6 Hz, benzene C_3-H).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_7S$: C, 43.25; H, 3.37; N, 7.21; Cl, 9.12; S, 8.25. Found: C, 43.24; H, 3.46; N, 7.11; Cl, 9.01; S, 8.06.

Ethyl 1-(2-Aminophenylsulfonyl)-1*H*-pyrrole-2-acetate (**7**).

To a mixture of **15** (8.5 g, 0.024 mole) and anhydrous sodium iodide (9.0 g, 0.040 mole) in dry acetonitrile (24 ml), chlorotrimethylsilane (6.1 ml, 5.4 g, 0.048 mole) was added dropwise with stirring over 20 minutes. During the addition, the reaction vessel was heated at 30-35°. After 30 minutes the reaction mixture was diluted with additional acetonitrile (12 ml) and acetic acid (2.4 ml). Next zinc dust (10.9 g, 0.168 mole) was added portionwise with stirring at room temperature and after 15 minutes the mixture was heated at 75-85° for 5 hours. After cooling, the mixture was filtered and the solid was washed with ethyl acetate (5 x 30 ml). The filtrate was washed with dilute sodium hydrogen carbonate solution (3 x 30 ml) and subsequently with sodium hydrogen sulfite solution (3 x 30 ml), then dried. After removal of solvent, the crude product was chromatographed on alumina column (ethyl acetate as eluent) to give pure **7** (3.4 g, 46% yield), mp 123-125° (from benzene); ir: 3500, 3390 cm^{-1} (NH_2) and 1730 (C=O); pmr (deuteriochloroform): δ 1.22 (t, 3H, CH_3), 3.77 (s, 2H, CH_2), 4.09 (q, 2H, OCH_2), 5.07 (s, broad, 2H, NH_2), 6.18 (m, 2H, pyrrole β-H), 6.64-6.72 (m, 2H, benzene C_3-H and C_5-H), 7.18-7.30 (m, 2H, pyrrole α-H and benzene C_4-H) and 7.55 (dd, 1H, J_o = 8.3 Hz, J_m = 1.1 Hz, benzene C_6-H).

Anal. Calcd. for $C_{14}H_{16}N_2O_4S$: C, 54.53; H, 5.23; N, 9.08; S, 10.40. Found: C, 54.50; H, 5.11; N, 9.15; S, 10.58.

Ethyl 1-(2-Amino-5-chlorophenylsulfonyl)-1*H*-pyrrole-2-acetate (**19**) and Ethyl 1-(2-Amino-5-chlorophenylsulfonyl)-1*H*-pyrrole-2-(α-hydroxy) acetate (**20**).

After **18** was allowed to react as above (time reaction, 2 hours), the reaction mixture was chromatographed (alumina, ethyl acetate). The first eluates afforded **19** in 36% yield, mp 122-124° (from benzene/cyclohexane); ir: 3470, 3360 cm^{-1} (NH_2) and 1735 (C=O); pmr (deuteriochloroform): δ 1.23 (t, 3H, CH_3), 3.80 (s, 2H, CH_2), 4.10 (q, 2H, OCH_2), 5.10 (s, broad, 2H, NH_2), 6.20 (m, 2H, pyrrole β-H), 6.62 (d, 1H, J_o = 8.8 Hz, benzene C_3-H), 7.17 (m, 1H, pyrrole α-H), 7.23 (dd, 1H, J_o = 8.8 Hz, J_m = 2.5 Hz, benzene C_4-H) and 7.52 (d, 1H, J_m = 2.5 Hz, benzene C_6-H).

Anal. Calcd. for $C_{14}H_{15}ClN_2O_4S$: C, 49.05; H, 4.41; N, 8.17; Cl, 10.34; S, 9.35. Found: C, 48.92; H, 4.39; N, 8.23; Cl, 10.22; S, 9.39.

Further elution afforded **20**, 27% yield, mp 109-111° (from benzene/cyclohexane); ir: 3470, 3360, 3230 cm^{-1} (NH_2 and OH) and 1730 (C=O); pmr (deuteriochloroform): δ 1.26 (t, 3H, CH_3), 3.51 (s, broad, 1H, OH), 4.27 (q, 2H, CH_2), 5.25 (s, broad, 2H, NH_2), 5.59 (s, 1H, CH), 6.23 (m, 2H, pyrrole β-H), 6.60 (m, 1H, J_o = 8.8 Hz, benzene C_3-H), 7.17-7.26 (m, 2H, pyrrole α-H and benzene C_4-H) and 7.65 (d, 1H, J_m = 2.4 Hz, benzene C_6-H).

Anal. Calcd. for $C_{14}H_{15}ClN_2O_5S$: C, 46.87; H, 4.21; N, 7.81; Cl, 9.88; S, 8.94. Found: C, 46.96; H, 4.02; N, 7.92; Cl, 9.75; S, 8.91.

1-(2-Aminophenylsulfonyl)-1*H*-pyrrole-2-acetic Acid (**5**).

A solution of **7** (2.5 g, 0.008 mole) in ethanol/tetrahydrofuran 1:1 (50 ml) was treated with aqueous 1*N* sodium hydroxide (8 ml, 0.008 mole) and the mixture was stirred at room temperature for 4.5 hours. Then the solution was poured onto crushed ice, treated with concentrated hydrochloric acid until *p*H 4 and extracted with ethyl acetate (3 x 100 ml). The organic extracts were collected, washed with brine (3 x 200 ml), dried and evaporated to give crude **5**, which was chromatographed on silica gel column (ethyl acetate/ethanol 9:1 as eluent), 2.2 g, 98% yield, mp 114-116° (from benzene); ir: 3480, 3380 cm^{-1} (NH_2) and 1720 (C=O); pmr (deuteriochloroform): δ 3.85 (s, 2H, CH_2), 6.19 (m, 2H, pyrrole β-H), 6.64-6.75 (m, 4H, benzene C_3-H and C_5-H and NH_2), 7.23-7.35 (m, 2H, pyrrole α-H and benzene C_4-H) and 7.54 (dd, 1H, J_o = 8.0 Hz, J_m = 1.1 Hz, benzene C_6-H).

Anal. Calcd. for $C_{12}H_{12}N_2O_4S$: C, 51.42; H, 4.32; N, 9.99; S, 11.44. Found: C, 51.49; H, 4.45; N, 9.80; S, 11.56.

1-(2-Amino-5-chlorophenylsulfonyl)-1*H*-pyrrole-2-acetic Acid (**21**).

This compound was prepared from **19** (2.7 g, 0.008 mole) as above (12 ml of 1*N* sodium hydroxide, stirring for 8 hours); **21** was obtained from chromatography (2.2 g, 87% yield), mp 173-175° (from toluene/ethanol); ir: 3480, 3380, 2950 cm^{-1} (NH_2 and OH) and 1720 (C=O); pmr (DMSO-d_6): δ 3.70 (s, 2H, CH_2), 6.22 (m, 2H, pyrrole β-H), 6.48 (s, broad, 2H, NH_2), 6.86 (d, 1H, J_o = 8.9 Hz, benzene C_3-H) and 7.35-7.47 (m, 3H, pyrrole α-H and benzene C_4-H and C_6-H).

Anal. Calcd. for $C_{12}H_{11}ClN_2O_4S$: C, 45.79; H, 3.52; N, 8.90; Cl, 11.26; S, 10.19. Found: C, 45.83; H, 3.59; N, 8.71; Cl, 11.39; S, 10.23.

10*H*-Pyrrolo[1,2-*b*][1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-Dioxide (**4**).

A solution of **5** (920 mg, 0.0033 mole) in dichloromethane (50 ml) was treated with *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (630 mg, 0.0033 mole) and dimethylaminopyridine (410 mg, 0.0033 mole). After stirring at room temperature for 6 days, water was added (50 ml) and the mixture was extracted with ethyl acetate (3 x 100 ml). The organic extracts were collected, washed with 1*N* hydrochloric acid (3 x 150 ml), brine (3 x 150 ml), saturated solution of sodium hydrogen carbonate (3 x 150 ml), brine again (3 x 150 ml) and then dried. Removal of solvent furnished a crude product, which was chromatographed on silica gel column (ethyl acetate as eluent) to give **4** (190 mg, 22% yield), mp 234-235° (from ethanol); ir: 3100 cm^{-1} (NH) and 1700 (C=O); pmr (DMSO-d_6): δ 3.36 (s, 2H, CH_2), 6.30 (m, 2H, pyrrole β-H), 7.39-7.44 (m, 2H, pyrrole α-H and benzene H near NH), 7.58-7.84 (m, 2H, benzene H), 8.10 (dd, 1H, J_o = 7.9 Hz, J_m = 2.0 Hz, benzene H near SO_2) and 10.47 (s, broad, 1H, NH).

Anal. Calcd. for $C_{12}H_{10}N_2O_3S$: C, 54.95; H, 3.84; N, 10.68; S, 12.22. Found: C, 55.02; H, 3.75; N, 10.73; S, 12.14.

7-Chloro-10*H*-pyrrolo[1,2-*b*][1,2,6]benzothiadiazocin-11(12*H*)-one 5,5-dioxide (**16**).

This compound was prepared from **21** as described above; **16** was obtained in 15% yield, mp 257-259° (from ethanol); ir: 3070 cm^{-1} (NH) and 1690 (C=O); pmr (deuteriochloroform): δ 3.54 (s, 2H, CH_2), 6.26 (m, 2H, pyrrole β-H), 7.34-7.41 (m, 2H, pyrrole α-H and benzene H near NH), 7.69 (dd, 1H, J_o = 8.4 Hz, J_m = 2.2 Hz, benzene H near Cl), 8.18 (d, 1H, J_m = 2.2 Hz, benzene H near SO_2) and 8.68 (s, broad, 1H, NH).

Anal. Calcd. for $C_{12}H_9ClN_2O_3S$: C, 48.57; H, 3.06; N, 9.44; Cl, 11.95; S, 10.80. Found: C, 48.39; H, 3.01; N, 9.31; Cl, 11.88; S, 10.84.

Ethyl Pyrrolo[1,2-*b*][1,2,5]benzothiadiazepine-11-carboxylate 5,5-Dioxide (**14**).

A stirred solution of **13** (1.5 g, 0.004 mole) in glacial acetic acid (20 ml) was heated at 60°, while iron powder (1.3 g, 0.023 mole) was added portionwise over 40 minutes. Then the solvent was eliminated and the residue was treated with crushed ice and ethyl acetate (3 x 100 ml); the upper phases were separated, collected, washed with brine (3 x 200 ml), dried and evaporated to obtain pure **14** (1.2 g, 100% yield), as an oil; ir: 1720 cm^{-1} (C=O); pmr (deuteriochloroform): δ 1.42 (t, 3H, CH_3), 4.45 (q, 2H, CH_2), 6.46 (m, 1H, pyrrole C_4-H), 7.17 (m, 1H, pyrrole C_3-H), 7.40-7.71 (m, 4H, pyrrole C_5-H and benzene H) and 7.99 (m, 1H, benzene H near SO_2).

Anal. Calcd. for $C_{14}H_{12}N_2O_4S$: C, 55.26; H, 3.97; N, 9.21; S, 10.53. Found: C, 55.12; H, 3.84; N, 9.27; S, 10.32.

1-(2-Nitrophenylsulfonyl)-2-(5-oxazolyl)-1*H*-pyrrole (**9**).

A solution of toluene4-sulfonylmethylisocyanide (720 mg, 3.7 mmoles) in 1,2-dimethoxyethane (3 ml) was added dropwise under a nitrogen stream into a well stirred suspension of potassium *tert*-butoxide (850 mg, 7.2 mmoles, 3 ml of the same solvent) cooled at -35°. After the addition was complete, the mixture was cooled at -45° and a solution of **8** (1.0 g, 3.5 mmoles) in 1,2-dimethoxyethane (6 ml) was added dropwise. The mixture was stirred at -45° for 1.5 hours, then methanol (9 ml) was added and the mixture was refluxed for 15 minutes more. Evaporation of the solvent gave a residue which was treated with water (10 ml), glacial acetic acid (0.4 ml) and extracted with ethyl acetate (3 x 20 ml). The extracts were collected, washed with brine (3 x 50 ml) and dried. Evaporation of the solvent gave a crude product, which was chromatographed on alumina column (chloroform as eluent) to afford pure **9** (1.1 g, 27% yield), mp 118-120° (from benzene); pmr (deuteriochloroform): δ 6.78 and 6.99 (2m, 2H, pyrrole β-H), 7.27-7.31 (m, 2H, benzene C_4-H and C_5-H), 7.47 (m, 1H, pyrrole α-H), 7.89-7.93 (m, 2H, benzene C_3-H and C_6-H), 8.22 (s, 1H, oxazole C_4-H) and 8.70 (s, 1H, oxazole C_2-H).

Anal. Calcd. for $C_{13}H_9N_3O_5S$: C, 48.90; H, 2.84; N, 13.16; S, 10.04. Found: C, 48.79; H, 2.91; N, 13.24; S, 10.00.

Acknowledgements.

We thank the Italian CNR and MURST for financial aid.

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