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A NEW CLASS OF FUSED BIS [1,2,3] SELENA AND/OR THIADIAZOLES

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A NEW CLASS OF FUSED *BIS*[1,2,3] SELENA AND/OR THIADIAZOLES

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ABSTRACT

A novel class of *bis* selena and/or thiadiazoles were prepared by the reaction of semicarbazones of 3,6-dithiaoctahydrophenanthrene-1,8-dione, 3,6-dithiaoctahydroanthracene-1,8-dione and 3,7-dithiaoctahydroanthracene-1,5-dione with SeO₂ and SOCl₂, respectively. The latter, in turn, were obtained from 1,2-, 1,3- and 1,4-xylylenedimercaptoacetic acids.

Over the years, a variety of mercaptoacetic acids have been used as intermediates in the synthesis of α,β -unsaturated compounds, carbocyclic and heterocyclic systems.^{1–13} Recently, the preparation of selena and thiadiazole fused heterocycles from arylmercaptoacetic acids have been reported.^{14,15} The present communication describes the use of 1,2-, 1,3- and 1,4- xylylenedimercaptoacetic acids (**4–6**) for the preparation of a new

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class of *bis* selena and/or thiadiazole units or mixed systems of selena and thiadiazole rings in one molecule, which hitherto not reported.

The synthetic scheme involves the cyclization of mercaptoacetic acids **4–6** with phosphorus pentoxide to obtain the respective diones **7–9**. Exposure of these diketones to two moles of semicarbazide hydrochloride followed by oxidative cyclization with selenium dioxide in acetic acid gave *bis* selenadiazoles, **12**, **16** and **20**. Similarly, the semicarbazone derivatives of **7–9** on Hurd–Mori reaction process¹⁶ with excess thionyl chloride afforded *bis* thiadiazoles **13**, **17** and **21**. On the other hand, reaction with selenium dioxide in acetic acid led to the formation of selenadiazoles, **10**, **14** and **18**. Formation of their semicarbazones followed by treatment with excess thionyl chloride furnished selena and thiadiazoles **11**, **15** and **19**. In summary, we here report a method for the preparation of *bis* selena/thiadiazoles or selena and thiadiazole units fused to dithiaoctahydroanthracene and phenanthrene diones (Scheme).

EXPERIMENTAL

Melting points were determined on a Mel–Temp apparatus and are uncorrected. The IR spectra were recorded on a Perkin–Elmer grating infrared spectrophotometer in KBr pellets. The ¹H NMR spectra were recorded at 200 MHz on a Bruker spectrospin and Varian EM-360 spectrometer in CDCl₃ with TMS as an internal standard. The purity of the compounds was checked by TLC (silica gel H, BDH hexane : ethyl acetate, 3 : 2). The microanalyses were performed by the Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh, India.

3,6-Dithiaoctahydrophenanthrene-1,8-dione(7)/ 3,6-Dithiaoctahydroanthracene-1,8-dione (8)/and 3,7-Dithiaoctahydroanthracene-1,5-dione (9)

General procedure: To a solution of dimercaptoacetic acid $4/5/6^{17-19}$ (1.6 g, 0.01 mol) in dry benzene (30 mL) an excess of phosphorus pentoxide (5 g) was added and the mixture refluxed for 6–8 h. The reaction was monitored at frequent intervals by TLC. After completion of the reaction the cooled content was extracted with benzene. The combined benzene extracts were washed with water, saturated sodium bicarbonate solution and again with water. The organic layer was dried over anhydrous sodium sulfate.

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BIS SELENA/THIADIAZOLES



(i) HSCH₂CO₂H/NaOH/MeOH; (ii)P₂O₅/benzene; (iii) 2NH₂NHCONH₂/NaOAc/MeOH (iv) SeO₂, AcOH, 60–70°C; (v)SOCl₂, CH₂Cl₂, -10° C, (vi) NH₂NHCONH₂/NaOAc/MeOH

Scheme.



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Evaporation of the solvent gave a crude product which was filtered through a column of silica gel (60-120 mesh) using ethyl acetate: hexane (2:3) eluents.

7: m.p: 152–153°C, Yield, 85%; IR: 1630 (C=O); ¹H NMR: δ , 3.78 (s, 4H, SCH₂), 4.16 (s, 4H, SCH₂CO), 7.14 (s, 2H, Ar-H), **8**: m.p. 167–168°C, Yield 82%, IR: 1640 (C=O); ¹H NMR: δ , 3.65 (s, 4H, SCH₂), 4.14 (s, 4H, SCH₂CO), 7.08 (s, 1H, Ar-H), 7.82 (s, 1H, Ar-H). **9**: m.p. 185–186°C, Yield 88%, IR: 1660 (C=O), ¹H NMR: δ , 3.68, (s, 4H, SCH₂), 4.25 (s, 4H, SCH₂CO), 6.99 (s, 2H, Ar-H).

3,6-Dithia-3,4,5,6-tetrahydrophenanthrene [1,2-d;7,8-d]bis[1,2,3]selenadiazole (12), 3,6-Dithia-3,4,5,6-tetrahydroanthracene [1,2-d;7,8-d]bis[1,2,3]selenadiazole (16) and 3,7-Dithia-3,4,7,8-tetrahydroanthracene-[1,2-d;5,6-d]bis[1,2,3]selenadiazole (20)

General procedure: The bis semicarbazone of 7/8/9 was prepared by refluxing 7/8/9 (1.25 g, 0.01 mol) with semicarbazide hydrochloride (2.22 g, 0.02 mol) and sodium acetate (2.72 g, 0.02 mol) in 20 ml of methanol. The reaction mixture was concentrated, cooled and poured into ice-cold water. The solid separated was filtered, washed with water, dried and recrystallized from ethanol to get pure sample, bis semicarbazone of 7: m.p. 195–197°C, yield 88%, bis semicarbazone of 8: m.p: 202-204°C, yield 80%; bis semicarbazone of 9: m.p. 207–209°C; yield 83%. To bis semicarbazones of 7/8/9 (1.3 g, 0.01 mol) in glacial acetic acid (10 mL), selenium dioxide (3.8 g, 0.02 mol) was added in portions and the mixture stirred until the evolution of gas ceased. The progress of the reaction was checked by TLC. After completion of the reaction, the mixture was allowed to attain room temperature. The deposited selenium was removed by filtration. The filtrate was poured onto crushed ice and the solid obtained was filtered, dried and purified through a column of silica gel (60–120 mesh) using ethyl acetate : hexane (1:3) as eluents.

12: m.p. 117–119°C, Yield, 62%; IR: 1440 (N=N); ¹H NMR: δ , 3.74 (s, 4H, SCH₂), 7.20 (s, 2H, Ar-H); Anal. Calcd. for C₁₂H₆N₄Se₂S₂: C, 33.65; H, 1.41; N, 13.20; Found: C, 33.84; H, 1.49; 13.20. **16**: m.p. 139–141°C, Yield 66%; IR 1460 (N=N); ¹H NMR: δ , 3.62 (s, 4H, SCH₂), 7.10 (s, 1H, Ar-H), 7.22 (s, 1H, Ar-H); Anal. Calcd. for C₁₂H₆N₄Se₂S₂: C, 33.65; H, 1.41, N, 13.08; Found: C, 33.54; H, 1.30; N, 13.00. **20**: m.p. 135–137°C, Yield 65%; IR: 1458 (N=N); ¹H NMR: δ , 3.48 (s, 4H, SCH₂), 7.15 (s, 2H,

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BIS SELENA/THIADIAZOLES

Ar-H); Anal. Calcd. for C₁₂H₆N₄Se₂S₂: C; 33.65, H, 1.41; N, 13.08; Found: C, 33.79; H, 1.48; N, 13.00.

3,6-Dithia-3,4,5,6,7,8-hexahydrophenanthrene [1,2-*d*] [1,2,3]selenadiazole-8-one (10), 3,6-Dithia-3,4,5,6,7,8hexahydroanthracene[1,2-*d*][1,2,3]selenadiazole-8-one (14) and 3,7-Dithia-3,4,5,6,7,8-hexahydroanthracene-[1,2-*d*][1,2,3]selenadiazole-5-one (18)

General procedure: The mono semicarbazone of 7/8/9 was prepared by refluxing 7/8/9 (1.25 g, 0.01 mol), semicarbazide hydrochloride (1.11 g, 0.01 mol) and sodium acetate (1.36 g, 0.01 mol) in methanol (20 mL). The work-up procedure was similar to *bis* semicarbazone of 7/8/9. Mono semicarbazone of 7: m.p. 175–177°C; yield 68%; mono semicarbazone of 8: m.p. 178–180°C, yield 74%; mono semicarbazone of 9: m.p. 194–196°C, yield 88%. The cyclization was carried out with mono semicarbazone of 7/8/9 (1.3 g, 0.01 mol) and selenium dioxide (1.9 g, 0.01 mol) in glacial acetic acid as mentioned above. The solid obtained was purified over a column of silica gel (60–120 mesh) using ethyl acetate : hexane (1:3) as eluents.

10: m.p. 129–131°C, Yield 72%; IR: 1645 (C=O), 1452 (N=N); ¹H NMR: δ , 3.68 (s, 4H, SCH₂), 4.24 (s, 2H, SCH₂CO), 7.11 (d, 1H, Ar-H, J=8.2 Hz), 7.18 (d, 1H, Ar-H, J=8.2 Hz); Anal. Calcd. for C₁₂H₈N₂OSeS₂: C, 42.47; H, 2.30; N, 8.25; Found: C, 42.26; 2.30; N, 8.12. **14**: m.p. 146–148°C, Yield 75%; IR: 1640 (C=O), 1460 (N=N); ¹H NMR: δ , 3.42 (s, 4H, SCH₂), 4.32 (s, 2H, SCH₂CO), 7.14 (s, 1H, Ar-H), 7.34 (s, 1H, Ar-H); Anal. Calcd. for C₁₂H₈N₂OSeS₂: C, 42.47, H, 2.37; N, 8.25; Found: C, 42.40; H, 2.42; N, 8.10. **18**: m.p. 137–139°C, Yield 62%; IR: 1620 (C=O), 1440 (N=N); ¹H NMR: δ , 3.42 (s, 4H, SCH₂), 4.18 (s, 2H, SCH₂CO), 6.99 (s, 1H, Ar-H) 7.16 (s, 1H, Ar-H); Anal. Calcd. for C₁₂H₈N₂OSeS₂: C, 42.47; H, 2.37; N, 8.25; Found: C, 42.27; H, 2.47; N, 8.39.

> 3,6-Dithia-3,4,5,6-tetrahydrophenanthrene[1,2-*d*; 7,8-*d*]*bis*[1,2,3]thiadiazole (13), 3,6-Dithia-3,4,5,6tetrahydroanthracene[1,2-*d*;7,8-*d*]*bis*[1,2,3] thiadiazole (17) and 3,7-Dithia-3,4,7,8tetrahydroanthracene[1,2-*d*;5,6-*d*]*bis* [1,2,3]thiadiazole (21)

General procedure: *Bis* semicarbazones of 7/8/9 (1.3 g, 0.01 mol) was added portion wise to well cooled excess thionyl chloride (10 mL) at -10° C.

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The mixture was then allowed to attain room temperature. Then, it was extracted with dichloromethane (10 mL) and treated with saturated sodium carbonate solution. The organic layer was separated and washed thoroughly with water and dried. The solvent was evaporated off and the gummy product formed was solidified on treatment with pet.ether (40–60°C). However, a pure sample was obtained on filtration through a column of silica gel (60–120 mesh) using ethyl acetate: hexane (1:3) as eluents.

13: m.p. 136–137°C; Yield 64%; IR: 1450 (N=N); ¹H NMR: δ , 3.76 (s, 4H, SCH₂), 7.38 (s, 2H, Ar-H); Anal. Calcd. for C₁₂H₆N₄S₄: C, 43.09; H, 1.80; N, 16.75; Found: C, 43.00; H, 1.86; N, 16.62. **17**: m.p. 154–155°C, Yield 70%; IR: 1445 (N=N); ¹H NMR: δ , 3.56 (s, 4H, SCH₂), 7.17 (s, 1H, Ar-H), 7.30 (s, 1H, Ar-H); Anal. Calcd. for C₁₂H₆N₄S₄: C, 43.09; H, 1.80; N, 16.75; Found: C, 43.29; H, 1.89; N, 16.64. **21**: m.p. 142–144°C, Yield 70%; IR: 1452 (N=N), ¹H NMR: δ , 3.45 (s, 4H, SCH₂), 7.12 (s, 2H, Ar-H); Anal. Calcd. for C₁₂H₆N₄S₄: C, 43.18; H, 1.75; N, 16.89.

3,6-Dithia-3,4,5,6-tetrahydrophenanthrene [1,2-*d*][1,2,3]selenadiazole[7,8-*d*][1,2,3]thiadiazole (11), 3,6-Dithia-3,4,5,6-tetrahydroanthracene[1,2-*d*][1,2,3] selenadiazole[7,8-*d*][1,2,3]thiadiazole (15) and 3,7-Dithia-3,4,7,8-tetrahydroanthracene[1,2-*d*][1,2,3] selenadiazole[5,6-*d*]thiadiazole (19)

General procedure: To a well cooled solution of thionyl chloride (5 mL), semicarbazone of **10/14/18** (1.1 g, 0.005 mol) was added in portions and stirred at -10° C and the process followed was same as above. The gummy substance obtained was solidified on treatment with pet. ether (40–60°C) which was purified through a column of silica gel (60–120 mesh) using ethyl acetate : hexane (1:3), as eluents.

11: m.p. 145–147°C, Yield 68%; IR: 1465 (N=N); ¹H NMR: δ , 3.74 (s, 2H, SCH₂), 7.22 (s, 2H, Ar-H); Anal. Calcd. for C₁₂H₆N₄SeS₃: C, 37.79; H, 1.58; N, 14.69; Found: C, 37.92; H, 1.66; N, 14.59. **15**: m.p. 153–155°C, Yield 72%; IR: 1458 (N=N); ¹H NMR: δ , 3.52 (s, 4H, SCH₂), 7.12 (s, 1H, Ar-H), 7.28 (s, 1H, Ar-H); Anal. Calcd. for C₁₂H₆N₄SeS₃: C, 37.79; H, 1.58; N, 14.69; Found: C, 37.59; H, 1.74; N, 14.80. **19**: m.p. 147–149°C, Yield 74%; IR: 1460 (N=N); ¹H NMR: δ , 3.45 (s, 4H, SCH₂); 7.12 (s, 2H, Ar-H); Anal. Calcd. for C₁₂H₆N₄SeS₃: C, 37.64; H, 1.70; N, 14.74.

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