Pergamon

Tetrahedron Letters, Vol. 35, No. 29, pp. 5279-5282, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)00980-5

Transformation of Isatin with P_4S_{10} to Pentathiepino[6,7-b]indole in One Step

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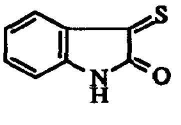
Abstract: Pentathiepino[6,7-b]indole (6) can be isolated from reactions of P_4S_{10} with isatin in pyridine. The structure of 6 has been determined with X-ray crystallography.

Although the two monothionated derivatives 1 and 2 (or its thiol tautomer) have been studied and discussed[1-5] in the literature neither isatindithione (3a) nor its tautomer 3b have been described, which most likely can be attributed to instability caused by the dithio functionality. Whereas the known thiolthione 4 is stable,[6] dithiones like dithiobenzil[7] (or its valence tautomer diphenyl-1,2-dithiete) are prone to dimerisations and other secondary reactions.[8] Nakayama[9] has recently shown that 1,2-dithiones (and 1,2-dithietes) can be stabilized by buttressing and/or resonance effects. The dithione 3 should be of interest as a "borderline" case.

In an attempt to obtain 3a (or its tautomer 3b) isatin was added to a refluxing solution of P_4S_{10} in pyridine (i.e. the zwitterionic reagent 5).[10,11] After aqueous work-up a semi-solid was obtained, which, after removal of S_8 with CS_2, extraction (hot toluene) and chromatography (SiO_2, CH_2Cl_2) gave a fast-running compound ($C_8H_5NS_5$) as light-yellow crystals (m.p. 170-171 °C, 7% yield), which could be recrystallized from toluene or acetonitrile. Spectroscopic data[12] further supported 6 as the assigned structure, which was later confirmed by X-ray crystallography.



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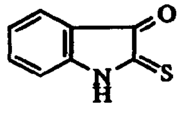

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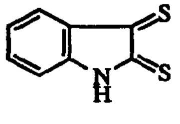

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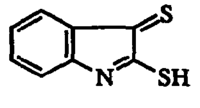

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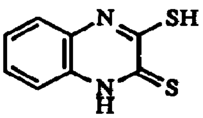

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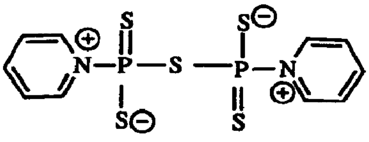

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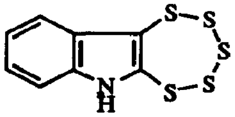

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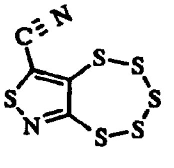

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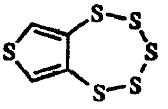

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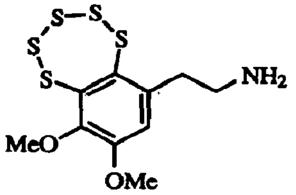

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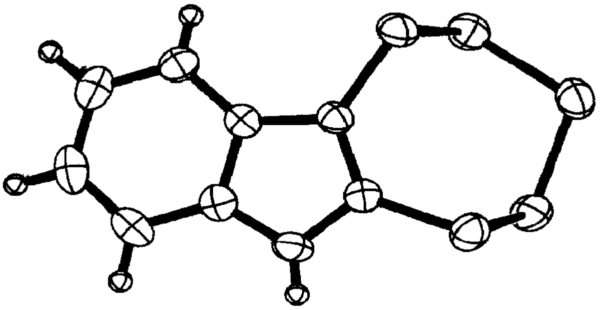
The formation of the pentathiepin **6** is rationalized in terms of reaction of •S-S$_x$-S• radicals with (the non-isolable) **3a**. Similar transformations[13] might explain the formation of benzopentathiepin from benzyne and S_8 (cf. also refs.[14-16]). Heterofused pentathiepins of related interest to **6** include compounds **7** and **8**, which have been prepared[17,18] from the corresponding dithiols and S_2Cl_2. It might be added that an increasing number of natural products featuring pentathiepin rings have been isolated (e.g. varacin **9** and several others).[19,20]

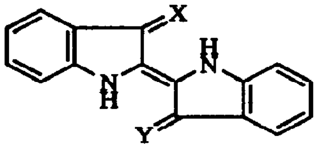


ORTEP plot of Pentathiepino[6,7-b]indole (6)

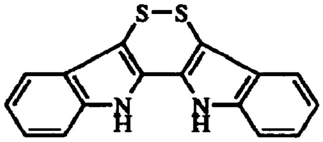
X-ray structure analysis: Compound **6** is monoclinic space group $P2_1/c$, a=8.8816(4), b=12.5663(9), c=10.0314(4) Å, β=107.55(1)°, V=1067.5(1) Å^3, D_{calc}=1.71 g cm^{-3} μ=10.0 cm^{-1}. A yellow prismatic crystal was mounted on a CAD4 Enraf-Nonius diffractometer with graphite monochromated Mo K_α radiation. Of the 2552 independent reflections ($\Theta<27.5°$), measured at 295° K, 1532 with $1>3\sigma(I)$ were used in the refinements. Two standard reflections remeasured every hour did not show any significant variation. Absorption correction by the ψ-scan method gave correction factors between 0.96 and 1.00. With anisotropic temperature factors for all non-hydrogen atoms R=0.030, wR=0.034 and GOF=1.2 were obtained.

Lists of atomic coordinates, thermal parameters, bond distances and angles and observed and calculated structure factors are available as Supplementary Material and have been deposited at the Cambridge Crystallographic Data Centre.

The initial experiments (addition of isatin to P_4S_{10} in refluxing pyridine) was now repeated at 85°C. After 5 minutes the reaction mixture was allowed to cool and the indigo (**10a**) formed was collected after 2 days (90% yield). This result is in harmony with the formation of **2**, followed by coupling and extrusion of sulfur, (cf. the last step in Sandmeyer's classical synthesis[2] of indigo). When the heating (85°C) was continued for 30 minutes the monothionated indigo derivative **10c**, as well as indirubin,[22] could be isolated by chromatography. Neither the fully thionated indigo derivative **10b** (cf. refs. 4 and 20) nor its valence tautomer **11** nor the pentathiepin **6** could be detected. The new compound **11** could readily be prepared by heating (reflux) 2,2'-biindolyl[23,24] with sulfur in DMF. The benzo[b]thiophene analogue of **11** has recently been prepared and the structure determined.[8a]



10a X=Y=O
b X=Y=S
c X=O, Y=S



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Our results indicate that isatin is quickly thionated by **5** yielding **2**, which has to be further thionated under appropriate conditions to **3** in order to give the pentathiepine **6**.

Acknowledgements: We thank Professor M. Guyot for communicating results prior to publication. Financial support from Carl Tryggers Stiftelse (to JB) is gratefully acknowledged.

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12. The pentathiepine **6** (m.p. 170-171 °C) gave the following data. IR (KBr): 3355, 1417(w), 1388, 1343, 1224, 815(w), 747(s), 658, 579, 534. MS: 275(14), 243(3), 211(100, $M-S_2$), 178(66), 146(21), 120(26), 64(53). ^{13}C NMR (DMSO): 112.4(d), 117.0(s), 119.3(d), 121.8(d), 124.3(d), 129.1(s), 135.1(s), 138.5(s).
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24. The red compound **11** gave the following data. IR (KBr): 3371, 3060, 1485(w), 1423, 1373, 1337, 1233, 1088, 746, 733, 571(w). MS: 295(28, M+1), 294(91, M), 262(100), 261(63), 232(53), 231(17), 100(67), 73(93).

(*Received in UK* 13 *April* 1994; *revised* 19 *May* 1994; *accepted* 20 *May* 1994)