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PREPARATION OF A STERICALLY HINDERED N-THIOSULFINYLANILINE AND ITS EQUILIBRIUM WITH A NOVEL HETEROCYCLE, 5H-1,2,3-DITHIAZOLE

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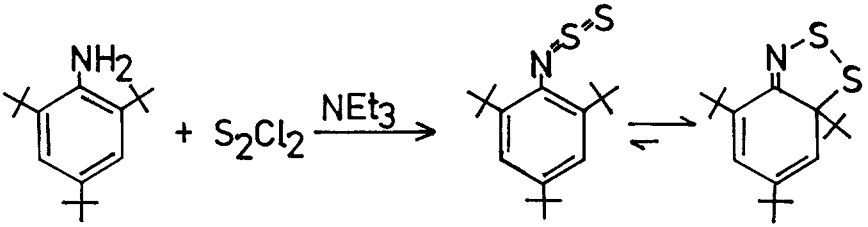
During the course of our studies on the abnormal reactions in poly-t-butylbenzene derivatives,[1] we have observed an interesting equilibrium between an N-thiosulfinylaniline system (2)[2] and its cyclic form, 5H-1,2,3-dithiazole (3), 3 represents the first example of this heterocyclic system, although some examples of 3H-1,2,3-dithiazoles have been reported[3]



1 2 3

Reaction of 2,4,6-tri-t-butylaniline (1)[4] with equimolar sulfur monochloride in the presence of triethylamine in ether at 0°C for 1 hr followed by dry column chromatography (silica gel, n-hexane) afforded a compound with a molecular formula $C_{18}H_{29}NS_2$ in 70% yield, m.p. 98.5-99.5°C (aq. ethanol); MS: m/e 323 (M^+, trace), 266 (72%), and 244 (100); molecular weight determined by vapor pressure osmometry in benzene at 40°C. 323[5] In solution, this compound is found to be a mixture of two tautomeric isomers (2 and 3) on the following basis; 1) the compound is yellow crystalline material but reddish in solution ($\lambda_{max}^{n\text{-hexane}}$. 240 (sh) ($\varepsilon$ 4720), 268 (2610), 292 (2580), 340 (2050), 410 nm (3480), and a very weak absorption at 535 nm)[6] and 2) the NMR spectrum shows the presence of two compounds, the major one 3 (CCl_4) δ 0.83 (s, 9H), 1.18 (s, 9H), 1.38 (s, 9H), 5.87 (d, J=2 Hz, 1H), and 6.39 (d, J=2 Hz, 1H), and the minor one 2 1.31 (s, 18H), 1.34 (s, 9H), and 7 34 (s, 2H). The molar ratio of the two was calculated based on the NMR signal intensity of the two olefinic protons of 3 and the two aromatic protons of 2 and found to vary reversibly with temperature The typical results are shown in the following table.

Temperature	[3]/[2]*	ΔG (Kcal/mol)
35°C	14.2	1.62
0°C	33.7	1.91

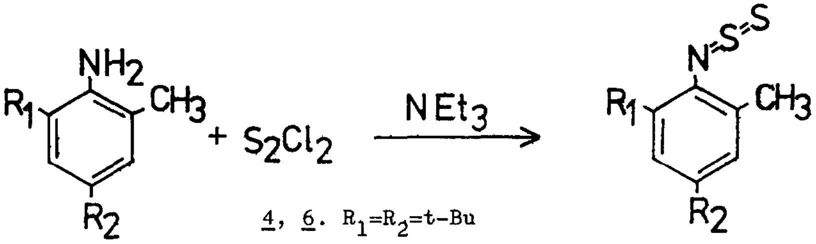
* Solvent. CD_2Cl_2; Concentration. 0.48 mol/l.

The unusual ring formation of 2 into 3 may be attributable primarily to decreased aromaticity due to steric congestion by the three bulky groups adjacent to each other and high reactivity of the thiosulfinyl group towards the unsaturated bond.[7,8] The cyclization can be considered to be cycloaddition of the -N=S=S group with a "double bond" of the benzene ring

Unlike the case of 1, a similar reaction with 2,4-di-t-butyl-6-methylaniline (4) gave the corresponding N-thiosulfinylaniline (6) in 81% yield, m.p. 67-68°C (aq. methanol), NMR (CCl_4) δ 1.33 (s, 18H), 2.02 (s, 3H), and 7.22 (AB q, J=2 Hz, $\Delta\delta$=0.22, 2H); UV: $\lambda_{max}^{n\text{-hexane}}$ 270 (sh) (ε 1470), 310 (sh) (1940), 343 (5590), 476 (2190), and 536 nm (sh) (1190); MS: m/e 247 (M^+-H_2S, 26%), 232 (100), and 204 (95).[5]

The reaction of 2,4,6-trimethylaniline (5) with sulfur monochloride under similar conditions as described in the reaction of 1 gave no N-thiosulfinylaniline However, lowering the reaction (-78°C, 2 hr) and work-up temperature (-2°C) made possible the isolation of 7 in 2% yield as a red purple oil, although we have not succeeded in the isolation of analytically pure specimen so far, NMR (CCl_4 at 0°C) δ 2.01 (s, 6H), 2 31 (s, 3H), and 6.90 (s, 2H), UV

$\lambda_{max}^{n\text{-}pentane}$ 336 (ε 5700), 462 (1900), 540 (sh) nm (870).



4, 6. $R_1=R_2=t\text{-}Bu$

5, 7. $R_1=R_2=CH_3$

4, 5

6, 7

Although reactions of sulfur monochloride with anilines leading to the formation of 1,3,2-benzothiazathiolium chloride are known as Herz reaction⁹⁾ and have been extensively studied, there has been no report on the reaction with anilines substituted at both ortho-positions The present results show the product in the latter case is an N-thiosulfinylaniline, although it is fairly unstable in the absence of enough steric protection

References and Notes

1) R Okazaki, Y Inagaki, and N. Inamoto, Chem. Letters, 1503 (1974), Y Inagaki, R. Okazaki, and N Inamoto, Bull. Chem Soc. Japan, 48, 621 (1975) and references cited therein.

2) Barton et al.⁷⁾ very recently reported the first example of an N-thiosulfinylaniline (i.e. p-dimethylamino-N-thiosulfinylaniline) from the corresponding nitroso (15%) and sulfinylamino compounds (1 1%) They also describe the preparation by the reaction of the corresponding aniline with sulfur monochloride but the formation of the N-thiosulfinylaniline was checked only by the electronic spectrum, the yield not being given.

3) L D. Huestis, M.L. Walsh, and N. Hahn, J. Org. Chem , 30, 2763 (1965) and references cited therein.

4) J Burgers, M A. Hoefnagel, P E Verkade, H. Visser, and B M. Wepster, Rec Trav. Chim., 77, 491 (1958)

5) Satisfactory analytical data have been obtained for this compound.

6) This absorption could be observed only in a fairly concentrated solution (ca. 2.5×10^{-2} mol/l). The absorption around 540 nm is considered to be characteristic of the N-thiosulfinylaniline; see Ref. 7 and the data on 6 and 7 in the text.

7) D.H R. Barton and M.J. Robson, J Chem. Soc. Perkin I, 1245 (1974)

8) 2,4,6-Tri-t-butyl-N-sulfinylaniline was found to have no tendency to isomeriz into its cyclized form. Y Inagaki, R. Okazaki, and N. Inamoto, unpublished results

9) W.K. Warburton, Chem Rev., 57, 1011 (1957), Q E. Thompson, Quart. Reports on Sulfur Chem., 5, 245 (1970).