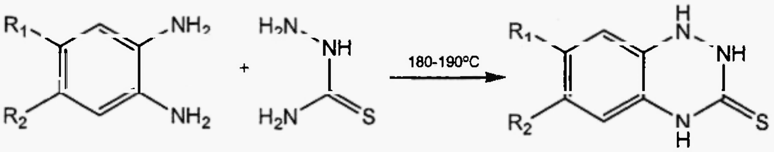
REINVESTIGATION OF *o*-PHENYLENEDIAMINE THERMAL CYCLOCONDENSATION WITH THIOSEMICARBAZIDE

M.Bakavoli*, E.Rezaei Seresht and M.Rahimizadeh
Department of Chemistry, School of Sciences, Ferdowsi University, Mashhad, Iran
e-mail : mbakavoli@yahoo.com

Abstract: Thermal cyclocondensation of *o*-phenylenediamine with thiosemicarbazide at elevated temperature gave the 1,3-dihydro-2H-1,3-benzimidazole-2-thione not the 1,4-dihydro- 1,2,4-benzotriazine-3(2H)thione claimed by an earlier worker. Analytical and spectral data are given in support of this reinvestitgation.

Introduction

The claim by Pujari (1) to have prepared 1,4-dihydro-1,2,4-benzotriazine-3(2H)thione **1a** by thermal condensation of *o*-phenylenediamines with thiosemicarbazide according to scheme1 is surprising.



$R_1 = R_2 = H$, Me

1a $R_1 = R_2 = H$

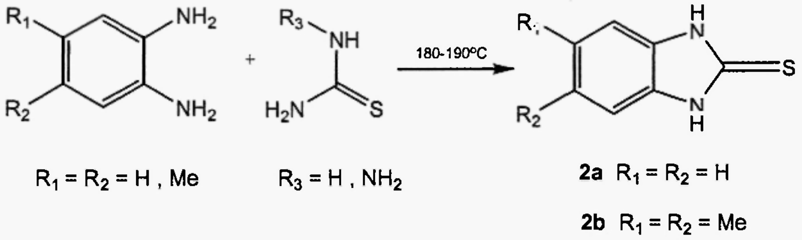
1b $R_1 = R_2 = Me$

Scheme-1

Pujari based his conclusion on the IR and ^1H NMR spectral analysis of his products without commenting on their mass spectra and microanalytical data, except for the percentage of sulfur that is given in the experimental part of his article. Even the ^1H NMR data provided is not convincing, since chemical shifts and the number of protons on nitrogens has not been given.The seemingly unusual reaction in scheme 1 and the lack of any information on its mechanism has been the reason for this reinvestigation.

Discussion

The reaction of *o*-phenylenediamine with thiosemicarbazide was reexamined. As reported, for instance, fusion of 4,5-dimethyl-*o*-phenylenediamine with thiosemicarbazide at 180-190°C gave a solid which was crystallized fromethanol as white flakes with melting point above 300°C. The molecular ion peak of this compound at 178m/z measured by EI mass spectrometry together with its microanalytical data (found: C,60.72; H,5.56; N,15.64; S,17.88%) are in obvious contrast with the proposed benzotriazine structure **1b** ($C_9H_{11}N_3S$) but in complete agreement with the benzimidazole ring system **2b** ($C_9H_{10}N_2S$). Further proof came from ^1H NMR studies of the fused products. For example, ^1H NMR spectrum of say **1b** which was recorded in DMSO-d_6 showed a singlet for methyl protons at δ 2.21 ppm, a singlet for two aromatic protons at δ 6.91 ppm and a broad signal for N-H protons at δ 12.34 ppm which was removed on deuteration. All these data was taken as evidence that the compound has been assigned the incorrect structure, and that it was the corresponding benzimidazole-2-thione **2b**. Furthermore this compound was made unambiguously by fusion of 4,5-dimethyl-*o*-phenylenediamine with thiourea (scheme 2), which had the same spectral and micro analytical data as the compound described.



Scheme-2

It does; however, appear that the products obtained by cyclocondensation of the mentioned *o*-phenylenediamines with thiosemicarbazide were samples of benzimidazole-2-thiones **2a-b** and not the claimed benzotriazine-3(2H) thiones **1a-b**.

Experimental

Melting points were recorded on an Electrothermal type 9100 melting point apparatus. The FT-IR Spectra were obtained on a 4300 Shimadzu Spectrometer as KBr disks. The ^{1}H NMR (100 MHz) spectra were recorded on Bruker AM100 Spectrometer in DMSO-d_6 solution. Mass Spectra were obtained from Varian CH-7 instrument at 70 eV. Elemental analysis was obtained on Thermo Finnigan Flash EA microanalyzer.

Compound derived from fusion of *o*-phenylenediamine with thiosemicarbazide or thiourea (2a). yield 45% ; mp 305°C (Lit.[2] mp 303-304 °C); *Anal.,* (Found: C , 55.62 ; H , 4.04 ; N , 18.59 ; S , 21.16%) ; IR(KBr) , 1180 (C=S) , 3220 cm^{-1} (NH) ; ^{1}H NMR (100 MHz , DMSO-d_6) δ 7.14 (s , 4H) , δ 12.58 (br , s , 2H[exch.]) ; Ms (EI) *m/z* 150 (M$^+$, 18%).

Compound derived from fusion of 4, 5-dimethyl-*o*-phenylenediamine with thiosemicarbazide or thiourea (2b). yield 42% ; mp 330°C (Lit.[3] mp 328°C); *Anal.,* (Found: C , 60.72 ; H , 5.56 ; N , 15.64 ; S , 17.88%) ; IR(KBr) , 1195 (C=S) , 3100 cm^{-1} (NH) ; ^{1}H NMR (100 MHz , DMSO-d_6) δ 2.21(s , 6H), δ 6.91 (s , 2H) , δ 12.34 (br , s , 2H[exch.]) ; Ms (EI) *m/z* 178 (M$^+$, 14%).

References:

1. S. Bala, M.L. Sachdeva, R.N. Handa and H.K. Pujari, Heterocycles, **14**, 149, (1980).
2. J.A. Van Allan and B.D. Deacon, Org. Synth. Coll. Vol. **4**, 569 (1963).
3. K. Takatori, Y. Yamada and O. Kawashima, J.Pharm.Soc.Japan, **75**, 881 (1955).

Received on November 11, 2005