ISSN 1070-4280, *Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 5, pp. 794–795. © Pleiades Publishing, Ltd., 2009.*
Original Russian Text © I.B. Rozentsveig, A.V. Popov, E.V. Kondrashov, G.G. Levkovskaya, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 5, p. 806.

SHORT COMMUNICATIONS

Unexpected Reaction of Dibenzyl Disulfide with Hydrazine

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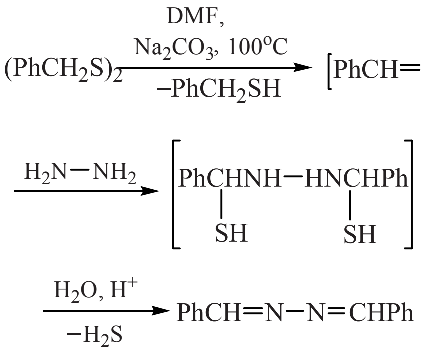
Received April 30, 2008

DOI: 10.1134/S1070428009050261

The reaction of hydrazine with dichalcogenides in aqueous alkaline medium is known to result in reductive cleavage of dichalcogenides giving thiols [1] and other chalcogenols [2], and hydrazine therewith is oxidized into nitrogen.

We found that the reaction of dibenzyl disulfide with excess hydrazine hydrochloride in DMF in the presence of sodium or potassium carbonates at heating to 100°C unexpectedly afforded benzalazine. The process was accompanied by hydrogen sulfide evolution.

It is presumable that under the conditions of the reaction the dibenzyl disulfide suffered 1,2-elimination with the formation of benzylthiol and thiobenzaldehyde. The latter underwent condensation with hydrazine to give the final benzalazine that apparently existed in the reaction mixture as thioaminal or hemiaminal, but was isolated at acidifying the reaction mixture in the individual state in 38% indicating a good yield of the intermediate thioaldehyde.



The examples are known of thiocarbonyl compounds generation from disulfides: for instance, thermolysis of dimethyl disulfide in a vacuum [3] or decomposition of alkaline water solutions of disulfides containing a labile hydrogen in the α-position [4, 5]. However no data on hydrazones formation in reaction of disulfides with hydrazine or its substituted derivatives were published.

The benzalazine formation was proved by comparison of the spectral characteristics and melting point of the isolated product with the properties of an authentic sample, and also was confirmed by elemental analysis.

Benzalazine. A mixture of 2.46 g (0.01 mol) of dibenzyl disulfide, 3.15 g (0.03 mol) of hydrazine hydrochloride, 3.18 g (0.03 mol) of sodium carbonate, and 5 ml of DMF was stirred for 20 h at 100°C. The reaction mixture was poured into 30 ml of water, filtered from excess dibenzyl disulfide, the filtrate was acidified with dilute HCl to pH 5–6 and left standing for 24 h. The precipitate was separated, washed with 5% HCl, then with water, and dried. Yield 0.79 g (38%), mp 91–93°C. IR spectrum, ν, cm^{-1}: 1625 (C=N), 2950 (CH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.62, 7.99 m (10H, C_6H_5), 8.82 s (2H, CH=N). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 121.30, 128.31, 128.86, 133.76 (C_6H_5), 161.37 (C=N). Found, %: C 81.03; H 5.73; N 13.62. $C_{14}H_{12}N_2$. Calculated, %: C 80.74; H 5.81; N 13.45.

^1H and ^{13}C were registered on a spectrometer Bruker DPX-400 (400.6, 100.61 MHz respectively), internal reference TMS.IR spectra were recorded on a spectrophotometr Bruker IFS-25 from samples pelletized with KBr.

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