NH_4OAc (2 g, 2.6 mmol). The reaction mixture was refluxed for 7 h and cooled to –20 °C, then methanol was added. The precipitate that formed was filtered off, washed with methanol, and dried to give compound **4c**.

4,5-Bis[*p*-(phenylethynyl)phenyl]-2-*p*-nitrophenyl)imidazole (4d). Compound **4d** was obtained similarly from 4,4'-di(phenylethynyl)benzil 3, *p*-nitrobenzaldehyde, and NH_4OAc.

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A new method for the synthesis of *N,N'*-thiobisamines

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Reaction of secondary amines (morpholine and piperidine) with sulfur and iodine afforded *N,N'*-thiobisamines in good yields.

Key words: *N,N'*-thiobisamines; secondary amines, reaction, sulfur, iodine.

The method of synthesis of *N,N'*-thiobisamines (**1a**) and *N,N'*-dithiobisamines (**1b**) by the reaction of sulfur chlorides with secondary amines is well known[1] (Scheme 1).

Scheme 1

$$\mathrm{RR'NH} + \mathrm{S}_n\mathrm{Cl}_2 \longrightarrow \underset{\mathbf{1a,b}}{\mathrm{RR'N{-}S}_n\mathrm{{-}NRR'}}$$

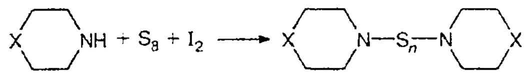
1: n = 1 (**a**), 2 (**b**)

The synthesis of compound **1a** by the reaction of amines with sodium thiosulfate and bromine at 5—10 °C has recently been reported.[2]

The products obtained, especially *N,N'*-thiobismorpholine and *N,N'*-dithiobismorpholine (**4a** and **4b**, respectively, Scheme 2), are used in industry as vulcanizers of rubber, stabilizers of oils, *etc.*[1]

We discovered that the reaction of secondary amines, *viz.*, morpholine (**2**) and piperidine (**3**), with sulfur and iodine afforded mono- and disulfides of amines **4a,b** and **5a,b** depending on the ratio of the starting reagents (Scheme 2).

Scheme 2



2, 3 → **4a,b, 5a,b**

2: X = O
3: X = CH_2

4: X = O, n = 1 (**a**), 2 (**b**)
5: X = CH_2, n = 1 (**a**), 2 (**b**)

We managed to obtain *N,N'*-thiobisamines **4a** (**5a**) in a good yield when no less than 8 equiv. of amine **2** (**3**) was taken for 1/8 equiv. of S_8 and 1 equiv. of iodine. The use of larger amounts of sulfur in this reaction resulted in the isolation of *N,N'*-dithiobisamines **4b** and **5b** in low yields since monosulfides **4a** and **5a** and,

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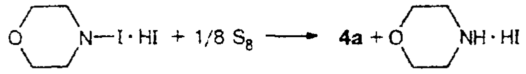
probably, higher sulfides of amines are also formed.

When the reaction was carried out in an excess of amine **2** (**3**) or in pyridine, the yield of compounds **4a** and **5a** was 60—70%, and in DMF the yield was ~30% ($(Me_2N)_2S$ was additionally formed). Resinification of the reaction mixture was observed in nitromethane, benzene, and toluene.

In the presence of an excess of morpholine the reaction proceeded through the intermediate formation of *N*-iodoamines, which was confirmed by the experiment with the independently prepared *N*-iodomorpholine hydroiodide (the adduct of iodine with morpholine)[3] (Scheme 3).

Scheme 3



Thus, we developed a laboratory procedure for the synthesis of *N,N'*-thiobisamines without recourse to sulfur dichloride, which is inconvenient to use.[4]

Experimental

Melting points were determined on a Koffler heating stage. ^{1}H NMR spectra were obtained of a Bruker WM-250 instrument (250 MHz).

***N,N'*-Thiobisamines (4a and 5a).** A mixture of sulfur (0.32 g, 1.25 mmol), amine **2** (**3**) (80 mmol) and pyridine (5 mL) was heated in a reflux condenser until the dissolution of the components. A solution of iodine (2.54 g, 10 mmol) in pyridine (10—15 mL) was added over 1 min to the reaction mixture with stirring. After several minutes of heating, the solution decolorized. The reaction mixture was concentrated *in vacuo*, the residue was mixed with water (50—70 mL), and the crystals formed were filtered off, washed three times with water, and dried to afford compound **4a** or **5a**.

***N,N'*-Thiobismorpholine (4a).** The yield was 63%, m.p. 125—126 °C (from MeOH) (*cf.* Ref. 1: m.p. 125 °C), R_f 0.44 (EtO_2, Silufol). Found (%): C, 47.51; H, 7.66; N, 13.78; S, 14.89. $C_8H_{16}N_2O_2S$. Calculated (%): C, 47.03; H, 7.89; N, 13.71; S, 15.69. ^{1}H NMR ($CDCl_3$,), δ: 3.25 (t, CH_2); 3.65 (t, CH_2).

***N,N'*-Thiobispiperidine (5a).** The yield was 71%, m.p. 74—75 °C (from MeOH—H_2O) (*cf.* Ref. 1: m.p. 74 °C), R_f 0.76 (Et_2O, Silufol).

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Resonance capture of electrons by molecules of substituted pyrans

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Negative-ion mass spectrometry in the mode of resonance capture of electrons and photoelectron spectroscopy in combination with quantum-chemical calculations showed that the formation of the resonance states of negative molecular ions in the reaction of electrons with molecules of substituted pyrans in the ultraviolet optical excitation energy region occurs according to the mechanism of intershell Feshbach resonance with the consecutive excitation of an electron from several higher occupied MO to one vacant MO. In a low-energy region, the resonance at 1.4 eV is a resonance of form and the resonance at 3—4 eV is the usual electron exciting Feshbach resonance with a parent triplet state $(\pi,\pi^*)^3$. The one and the same vacant π^*_{CC} MO is "active" in all the resonances mentioned.

Key words: molecular orbital, resonance state; resonance capture of electrons; photoelectron spectroscopy.

The efficiency of the earlier proposed method[1] of interpretation of resonance states (RS) of negative molecular ions (NMI) that involves the combined application of negative ions (NI) mass spectrometry in the

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