onto ice (~100 g). The precipitate that formed was filtered off, washed with a small amount of water, dried in air, and crystallized from hexane to give 0.18 g (85%) of tribromide 4, m.p. \$1-\$3 °C, R_f 0.64. ¹³C NMR (CDCl₃), \$: 140.7 (C(3)); 116.6 (C(4)); 136.4 (C(5)). Found (%): C, 11.96; Br, 74.60; N, 4.32; S, 9.83. C₃Br₃NS. Calculated (%): C, 11.19; Br, 74.51; N, 4.35; S, 9.95.

3,4-Dibromo-5-iodoisothiazole (5). lodine (0.20 g, 0.79 mmol) was added to a solution of 3,4-dibromoisothiazole 2 (0.28 g, 1.15 mmol) in concentrated H_2SO_4 (10 mL) at 20 °C with stirring and after 30 min NaIO₄ (0.12, 0.56 mmol) was added in small portions to the reaction mixture. The reaction mixture was stirred at 30 °C for 4 h and at 80-90 °C for 4 h, cooled to 20 °C, and poured onto ice (~100 g). The mixture was decolorized with Na2SO3 and extracted with CHCl₃ (3×10 mL). The combined organic extracts were washed with water (2×10 mL) and dried with MgSO₄. The solvent was removed and the residue was crystallized three times from hexane to obtain 0.10 g (23%) of compound 5, m.p. 154–157 °C, R_f 0.56. ¹³C NMR (CDCl₃), δ : 139.7 (C(3)); 122.3 (C(4)); 104.0 (C(5)). Found (%): C, 10.31; Br, 43.29; I, 34.36; N. 3.71; S, 8.67. C₃Br₂INS. Calculated (%): C, 9.76; Br, 43.34; I, 34.42; N, 3.80; S, 8.68.

3-Bromo-4,5-diiodoisothiazole (6). Iodine (0.63 g, 2.36 mmol) was added to a solution of 3-bromo-4-iodoisothiazole 3 (1.67 g, 6.76 mmol) in concentrated H_2SO_4 (50 mL) at 20 °C with stirring and after 30 min NaIO₄ (0.39, 1.64 mmol) was added in small portions to the reaction mixture. The dark solution that formed was stirred at 20 °C for 2 h and kept at 70 °C for 24 h. The reaction mixture was poured onto ice (~100 g) and decolorized with Na₂SO₃. The residue was filtered, washed with water (~100 mL), dried in air, and crystallized three times from CHCl₃ to obtain 1.47 g (61%) of compound **6**, m.p. 168–169 °C, $R_{\rm f}$ 0.56. ¹³C NMR (DMSO-d₆), δ : 144.7 (C(3)); 117.2 (C(4)); 101.0 (C(5)). Found (%): C, 8.82; Br, 19.48; I, 61.74; S, 7.80. C₃BrI₂NS. Calculated (%): C, 8.66; Br, 19.22; I, 61.05; S, 7.70.

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Improved synthesis of bis[p-(phenylethynyl)phenyl]hetarylenes

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Bis[p-(phenylethynyl)phenyl]hetarylenes were synthesized in high yields by an improved method using cross-coupling between phenylacetylene and 4,4'-dibromobenzil followed by condensation of the 4,4'-di(phenylethynyl)benzil obtained with either *o*-phenylenediamine and 3,4-diaminobenzoic acid or with benzaldehyde and *p*-nitrobenzaldehyde in the presence of ammonium acetate.

Key words: phenylacetylene, cross-coupling reaction, dibromobenzil; bis[*p*-(phenyl-ethynyl)phenyl]hetarylenes.

Earlier, we developed a method for the synthesis of $bis[p-phenylethynyl)phenyl]hetarylenes^1 using Pd-cata$ lyzed cross-coupling² of heterocyclic dibromides prepared from 4,4'-dibromobenzil (1)³ with a twofold molarexcess of phenylacetylene (Scheme 1, pathway A). The major disadvantage of this method is the low activity of heteroaromatic dibromides 2a-d in the crosscoupling reactions; this results in small yields of bis[*p*-(phenylethynyl)phenyl]hetarylenes 4a-d (Table 1). The low activity of heteroaromatic dibromides is associated

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Scheme 1



with the slightly pronounced electron-withdrawing properties of heterocycles.⁴

To overcome this disadvantage we modified the method of synthesis of bis[p-(phenylethynyl)phenyl]hetarylenes by changing the sequence of the transformations of the original compound 1 (see Scheme 1, path $way B). Since <math>\alpha$ -diketone groups are strong electron acceptors, ^{5,6} the cross-coupling reaction of dibromide 1 with a twofold molar excess of phenylacetylene occurs very easily to give 4,4'-di(phenylethynyl)benzil (3) in high yield (see Table 1). In the IR spectra of compound 3, there is an absorption bond at 1680 cm⁻¹, which is typical of stretching vibrations of α -dicarbonyl groups. Further transformations of diketone 3 into bis[p-(phenyl-

Table 1. Properties of compounds 3 and 4a-d

Compo- und	Yield (%)	M.p./°C H (solvent)	Raman spectrum, v(C≡C)/cm ⁻¹
3	91	182-184	2214
4a	20* 96**	209—210 (DMF)	2212
4b	19* 81**	306—307 (DMF)	2215
4c	21* 79**	254—256 (DMF)	2219
4d	34* 96**	267—269 (DMF)	2218

* Yield (method A). ** Yield (method B).

ethynyl)phenyl]hetarylenes 4a-d also occurred in high yields (see Table 1) to give products identical to those described previously.¹ In their Raman spectra, there are absorption bands in the region 2212-2219 cm⁻¹, which are typical of stretching vibrations of the C=C bond.

Experimental

Raman spectra were recorded on a U 1000 spectrometer with excitation by 5145 Å from an ILA-2 100 MW Ar⁺-laser. IR spectra were obtained on a UR-20 for samples in Vaseline oil. The solvents and phenylacetylene were purified by standard procedures.

4,4'-Di(phenylethynyl)benzil (3) was obtained by a procedure reported earlier.³

2,3-Bis[p-(phenylethynyl)phenyl]quinoxaline (4a). Chloroform (20 mL) and methanol (2 mL) were added to a mixture of 4,4'-di(phenylethynyl)benzil 3 (1.025 g, 2.5 mmol) and o-phenylenediamine (0.2704 g, 2.5 mmol) under argon. The reaction mixture was stirred for 24 h at ca. 20 °C, and the resulting solution was concentrated to dryness to give compound 4a.

2,3-Bis[p-(phenylethynyl)phenyl]-6-carboxyquinoxaline (4b). m-Cresol (6 mL) was added to a mixture of 4,4'-di(phenylethynyl)benzil (3) (1.025 g, 2.5 mmol) and 3,4-diaminobenzoic acid under argon. The reaction mixture was heated at 150 °C for 5 h and cooled to ca. 20 °C; then methanol was added. The precipitate that formed was filtered off, washed with methanol, and dried to give compound 4b.

4,5-Bis[p-(phenylethynyl)phenyl]-2-phenylimidazole (4c). Acetic acid (16 mL) was added to a mixture of 4,4'-di(phenylethynyl)benzil (3) (1.066 g, 2.6 mmol), benzaldehyde 4, and NH₄OAc (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(phenyl-ethynyl)benzil 3, p-nitrobenzaldehyde, and NH₄OAc.

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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 $N_i N'$ -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 known¹ (Scheme 1).

Scheme 1

$$I: n = 1$$
 (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).



2:
$$X = 0$$
4: $X = 0, n = 1$ (a), 2 (b)**3:** $X = CH_2$ **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 S₈ 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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