ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 3, pp. 423–425. © Pleiades Publishing, Ltd., 2012.
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Synthesis and Properties of *trans*-2-[2-(2-Hetaryl)vinyl]benzothiazoles

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Received June 1, 2011

Abstract—Electrophilic substitution reactions (formylation and acylation) in the series of 2-[2-(2-furyl)vinyl]- and 2-[2-(2-thienyl)vinyl]benzothiazoles leads to the corresponding derivatives at the α-position of the furan or thiophene ring. The presence of a vinylene bridge weakens deshielding effect of the benzothiazole fragment on π-excessive heterocycles, so that such compounds react at a higher rate and under milder conditions as compared to hetarylbenzothiazoles having no vinylene bridge.

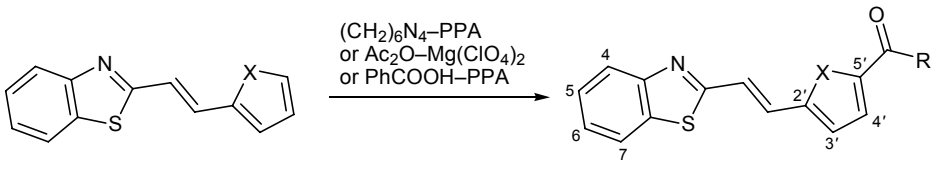
DOI: 10.1134/S1070428012030141

Introduction of substituents containing an extended π-system into benzazole molecules favors increase in quantum yield. Examples are benzothiazolyl stilbenes containing benzene and pyridine rings, which are used as optical bleaching agents. We previously studied [1] the electronic structure and spectral parameters of carbonyl derivatives of fused 2-hetarylbenzimidazoles. In the present work we examined methods of synthesis of 2-[2-(2-hetaryl)vinyl]benzothiazoles **I** and **II** containing a furan or thiophene ring and some their electrophilic substitution reactions (formylation, acylation) leading to potential luminophores.

Compounds **I** and **II** were synthesized previously in 22 and 65% yield, respectively, by reaction of 2-methylbenzothiazole with the corresponding aldehydes in the presence of fused zinc chloride [2]. However, we obtained better results by condensation of *o*-aminobenzenethiol with the corresponding hetarylacryloyl chlorides in 1-methylpyrrolidin-2-one. The yields of **I** and **II** were 56 and 78%, respectively. Compounds **I** and **II** were then brought into reactions with electrophilic reagents, hexamethylenetetramine in polyphosphoric acid (PPA), acetic anhydride and $Mg(ClO_4)_2$, and benzoic acid in PPA.

As shown in [3], the presence of a bridge connecting two heteroaromatic systems, e.g., of a CH=CH bridging moiety in 2-[2-(2-furyl)vinyl]benzimidazole, sharply weakens the effect of the imidazole ring on the reactivity of furan or other hetaryl fragment. This was confirmed by quantum-chemical calculation of the total (σ+π)-electron charges in the furan ring of 2-(2-hetarylvinyl)-substituted benzimidazoles and their analogs having no vinylene bridging group. A similar pattern was observed for 2-(2-hetarylvinyl)-benzothiazoles **I** and **II**. Analysis of the ^{1}H NMR data revealed a clearly defined correlation between the downfield shift of signals from 3-H of the hetaryl ring (which is determined mainly by the inductive effect) and deshielding effect of the benzothiazole fragment in 2-(2-furyl)- and 2-(2-thienyl)benzothiazoles (δ 7.20 and 7.51 ppm, respectively) [4]; the corresponding signals appeared in the spectra of compounds **I** and **II**

Scheme 1.



I, **II** **IIIa–IIIc**, **IVa–IVc**

I, **III**, X = O; **II**, **IV**, X = S; R = H (**a**), Me (**b**), Ph (**c**).

at δ 6.59 and 7.25 ppm (weaker deshielding). Therefore, we expected enhancement of the relative reactivity of the hetaryl ring in compounds **I** and **II** toward medium-strength electrophiles.

2-(2-Furyl)benzothiazole is known to undergo formylation according to Vilsmeier–Haack [2]. Likewise, compound **I** smoothly reacted under mild conditions with the DMF–$POCl_3$ complex to afford 86% of 5-formyl derivative **IIIa**. Compound **II** failed to react with DMF–$POCl_3$; therefore, we followed a different procedure which was successfully used previously to obtain formyl-substituted hetarylbenzimidazoles. The reaction of **II** with hexamethylenetetramine in polyphosphoric acid gave the corresponding aldehyde **IVa** in 67% yield (Scheme 1).

Unlike analogous benzimidazoles, compounds **I** and **II** were acetylated according to Dorofeenko [5], i.e., by heating in acetic anhydride containing a catalytic amount of magnesium perchlorate. Methyl ketones **IIIb** and **IVb** were obtained in 66 and 43% yield, respectively. We tried different methods for the benzoylation of compounds **I** and **II**, including many modifications of the Friedel–Crafts reaction; however, most of them gave no positive results. While searching for most appropriate reaction conditions and taking into account known data on successful benzoylation of analogous benzimidazoles, we resorted to the procedure proposed by Gardner [6] for the acylation of phenols and phenyl ethers. According to this procedure, compounds **I** and **II** were treated with benzoic acid in PPA at a relatively low temperature (80–100°C; hetarylbenzothiazoles having no vinyl group were subjected to benzoylation at 170–180°C [4]). As a result, phenyl ketones **IIIc** and **IVc** were synthesized in 77 and 63% yield, respectively.

Solutions of compounds **IIIa**–**IIIc** and **IVa**–**IVc** in ethanol and benzene showed strong fluorescence upon UV irradiation; therefore, these compounds were presumed to possess photoluminescent properties.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75 IR spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Varian Unity 300 instrument at 300 MHz from solutions in $CDCl_3$ using tetramethylsilane as internal reference. The progress of reactions was monitored by TLC on aluminum oxide of activity grade II according to Brockmann using methylene chloride or chloroform as eluent; spots were developed by treatment with iodine vapor. The elemental compositions were determined on a Perkin Elmer 2400 analyzer. The melting points were measured in capillaries using a PTP melting point apparatus.

2-[2-(2-Furyl)vinyl]-1,3-benzothiazole (I). 2-(2-Furyl)prop-2-enoyl chloride, 1.57 g (10 mmol), was added to a solution of 1.25 g (10 mmol) of *o*-aminobenzenethiol in 10 ml of 1-methylpyrrolidin-2-one. The mixture was heated for 1 h under reflux, cooled, and poured into 50 ml of cold water. The precipitate was filtered off, thoroughly washed with cold water, and recrystallized from ethanol. Yield 1.27 g (56%), mp 89– 90°C; published data [7]: mp 92–93°C. ^{1}H NMR spectrum, δ, ppm: 6.48–6.50 m (1H, 4′-H), 6.59 d (1H, 3′-H, J = 3.4 Hz), 7.26 d (1H, 2′-CH, J = 16.0 Hz), 7.36 t (1H, 6-H, J = 8.0 Hz), 7.37 d (1H, 2-CH, J = 16.0 Hz), 7.47 t (1H, 5-H, J = 8.0 Hz), 7.50 d (1H, 5′-H, J = 1.6 Hz), 7.85 d (1H, 7-H, J = 8.0 Hz), 7.98 d (1H, 4-H, J = 8.0 Hz).

2-[2-(2-Thienyl)vinyl]-1,3-benzothiazole (II) was synthesized in a similar way from 1.73 g (10 mmol) of 2-(2-thienyl)prop-2-enoyl chloride. Yield 1.90 g (78%), mp 116–117°C (from ethanol); published data [7]: mp 117°C. ^{1}H NMR spectrum, δ, ppm: 7.07 t (1H, 4′-H, J = 5.1 Hz), 7.21 d (1H, 2′-CH, J = 15.9 Hz), 7.25 d (1H, 3′-H, J = 3.3 Hz), 7.35 d (1H, 5′-H, J = 5.8 Hz), 7.36 t (1H, 6-H, J = 7.5 Hz), 7.47 t (1H, 5-H, J = 7.7 Hz), 7.67 d (1H, 2-CH, J = 15.9 Hz), 7.85 d (1H, 7-H, J = 8.2 Hz), 7.98 d (1H, 4′-H, J = 8.2 Hz).

5-[2-(1,3-Benzothiazol-2-yl)vinyl]furan-2-carbaldehyde (IIIa). Compound **I**, 1.14 g (5 mmol), was dissolved in 4.38 g (60 mmol) of *N*,*N*-dimethylformamide. The solution was cooled to 0°C, 4.61 g (30 mmol) of phosphoryl chloride was added dropwise at such a rate that the temperature did not exceed 10°C, and the mixture was stirred for 10 min at 0°C and for 2 h at 80°C, poured into 50 ml of water, and carefully neutralized with concentrated aqueous ammonia to pH 7–8. The product was extracted into chloroform (2×25 ml) and was subjected to column chromatography (20×3 cm; 50 g Al_2O_3; eluent methylene chloride). Yield 1.10 g (86%), mp 138–139°C (from ethanol). IR spectrum: ν 1680 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 6.74 d (1H, 3′-H, J = 3.6 Hz), 7.28 d (1H, 4′-H, J = 3.6 Hz), 7.38 d (1H, 2-CH, J = 15.8 Hz), 7.40 t (1H, 6-H, J = 8.0 Hz), 7.50 t (1H, 5-H, J = 8.0 Hz), 7.56 d (1H, 2′-H, J = 15.8 Hz), 7.87 d (1H, 7-H, J = 7.8 Hz), 8.04 d (1H, 4-H, J = 8.1 Hz), 9.67 s (1H, CHO). Found, %: C 66.14; H 3.79; N 5.25. $C_{14}H_9NO_2S$. Calculated, %: C 65.87; H 3.55; N 5.49.

5-[2-(1,3-Benzothiazol-2-yl)vinyl]thiophene-2-carbaldehyde (IVa). A mixture of 1.22 g (5 mmol) of compound **II** and 2.8 g (20 mmol) of hexamethylenetetramine in 20 g of PPA was heated for 2 h at 60–80°C. The mixture was then diluted with 50 ml of water and carefully neutralized with a solution of ammonia. The precipitate was filtered off and recrystallized. Yield 0.91 g (67%), mp 148–149°C (from ethanol). IR spectrum: ν 1660 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 7.31 d (1H, 3′-H, J = 3.9 Hz), 7.38 d (1H, 2′-CH, J = 15.8 Hz), 7.39 t (1H, 6-H, J = 7.8 Hz), 7.49 t (1H, 5-H, J = 7.8 Hz), 7.64 d (1H, 2-CH, J = 15.8 Hz), 7.70 d (1H, 4′-H, J = 3.9 Hz), 7.87 d (1H, 7-H, J = 7.8 Hz), 8.00 d (1H, 4-H, J = 7.8 Hz), 9.89 s (1H, CHO). Found, %: C 62.17; H 3.12; N 4.92. $C_{14}H_9NOS_2$. Calculated, %: C 61.97; H 3.34; N 5.16.

1-{5-[2-(1,3-Benzothiazol-2-yl)vinyl]furan-2-yl}-ethanone (IIIb). Compound **I**, 1.14 g (5 mmol), was dissolved in 15 ml of acetic anhydride, 0.01 g (0.04 mmol) of $Mg(ClO_4)_2$ was added, and the mixture was heated for 0.5 h under reflux. The mixture was then poured into 50 ml of cold water, and the product was isolated as described above for **IIIa**. Yield 0.89 g (66%), mp 138–139°C. IR spectrum: ν 1640 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 2.54 s (3H, CH_3), 6.69 d (1H, 3′-H, J = 3.6 Hz), 7.23 d (1H, 4′-H, J = 3.6 Hz), 7.38 d (1H, 2-CH, J = 15.8 Hz), 7.39 t (1H, 6-H, J = 7.8 Hz), 7.50 t (1H, 5-H, J = 8.0 Hz), 7.52 d (1H, 2′-CH, J = 15.8 Hz), 7.88 d (1H, 7-H, J = 8.0 Hz), 8.02 d (1H, 4-H, J = 8.0 Hz). Found, %: C 67.17; H 3.88; N 5.43. $C_{15}H_{11}NO_2S$. Calculated, %: C 66.90; H 4.12; N 5.20.

1-{5-[2-(1,3-Benzothiazol-2-yl)vinyl]thiophen-2-yl}ethanone (IVb) was synthesized in a similar way from 1.22 g (5 mmol) of compound **II**. Yield 0.61 g (43%), mp 168–169°C (from ethanol). IR spectrum: ν 1660 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 2.55 s (3H, CH_3), 7.23 d (1H, 3-H, J = 4.2 Hz), 7.32 d (1H, 2′-CH, J = 15.9 Hz), 7.38 t (1H, 6-H, J = 7.8 Hz), 7.47 t (1H, 5-H, J = 7.8 Hz), 7.60 d (1H, 2-CH, J = 15.9 Hz), 7.60 d (1H, 4′-H, J = 4.2 Hz), 7.85 d (1H, 7-H, J = 7.8 Hz), 7.99 d (1H, 4-H, J = 7.8 Hz). Found, %: C 62.81; H 4.15; N 5.23. $C_{15}H_{11}NOS_2$. Calculated, %: C 63.13; H 3.89; N 4.91.

{5-[2-(1,3-Benzothiazol-2-yl)vinyl]furan-2-yl}-phenylmethanone (IIIc). Benzoic acid, 2.44 g (20 mmol), was added to a solution of 1.14 g (5 mmol) of compound **I** in 20 g of PPA, and the mixture was stirred for 2 h at 80–100°C. The mixture was decomposed with 50 ml of water and neutralized with a concentrated solution of ammonia. The product was extracted into chloroform and isolated by chromatography on aluminum oxide using methylene chloride as eluent. Yield 1.27 g (77%), mp 108–109°C (from ethanol). IR spectrum: ν 1670 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 6.70 d (1H, 3′-H, J = 3.7 Hz), 7.21 d (1H, 4′-H, J = 3.7 Hz), 7.36 d (1H, 2-CH, J = 15.9 Hz), 7.38 t (1H, 6-H, J = 8.0 Hz), 7.48 t (1H, 5-H, J = 8.0 Hz), 7.50 d (1H, 2′-CH, J = 15.9 Hz), 7.56 t (3H, *m*-H, *p*-H, J = 7.7 Hz), 7.85 d (1H, 7-H, J = 8.0 Hz), 8.02 d (1H, 4-H, J = 8.0 Hz), 8.07 d (2H, *o*-H, J = 7.8 Hz). Found, %: C 72.77; H 4.23; N 4.47. $C_{20}H_{13}NO_2S$. Calculated, %: C 72.49; H 3.95; N 4.23.

{5-[2-(1,3-Benzothiazol-2-yl)vinyl]thiophen-2-yl}phenylmethanone (IVc) was synthesized in a similar way from 1.22 g (5 mmol) of compound **II**. Yield 1.09 g (63%), mp 150–151°C (from ethanol). IR spectrum: ν 1660 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 7.21 d (1H, 3′-H, J = 4.5 Hz), 7.31 d (1H, 2′-CH, J = 16.0 Hz), 7.38 t (1H, 6-H, J = 7.8 Hz), 7.45 t (1H, 5-H, J = 7.8 Hz), 7.54 t (3H, *m*-H, *p*-H, J = 7.8 Hz), 7.59 d (1H, 2-CH, J = 16.0 Hz), 7.61 d (1H, 4′-H, J = 4.5 Hz), 7.83 d (1H, 7-H, J = 7.8 Hz), 7.98 d (1H, 4-H, J = 7.8 Hz), 8.10 d (2H, *o*-H, J = 8.0 Hz). Found, %: C 68.83; H 4.08; N 3.76. $C_{20}H_{13}NOS_2$. Calculated, %: C 69.14; H 3.77; N 4.03.

REFERENCES

1. Roshal', A.D., Luk'yanov, B.S., and El'chaninov, M.M., *Zh. Fiz. Khim*., 2003, vol. 77, p. 1899.
2. Kornilov, M.Yu., Ruban, E.M., Fedchuk, V.N., Starinskaya, E.V., and Buznik, M.V., *Zh. Org. Khim*., 1973, vol. 9, p. 2577.
3. El'chaninov, M.M., *Doctoral (Chem.) Dissertation*, Rostov-on-Don, 2006.
4. Mel'nikova, E.B., El'chaninov, M.M., Milov, A.A., and Luk'yanov, B.S., *Khim. Geterotsikl. Soedin*., 2008, p. 1331.
5. Dorofeenko, G.N., *Zh. Obshch. Khim*., 1961, vol. 31, p. 994.
6. Gardner, P.D., *J. Am .Chem. Soc*., 1954, vol. 76, p. 4550.
7. Ried, W. and Hinsching, S., *Justus Liebigs Ann. Chem*., 1956, vol. 600, p. 47.