New 2-(benzothiazol-2-yl)-1,3-tropolones derived from 3,4,5,6-tetrachloro-1,2-benzoquinone

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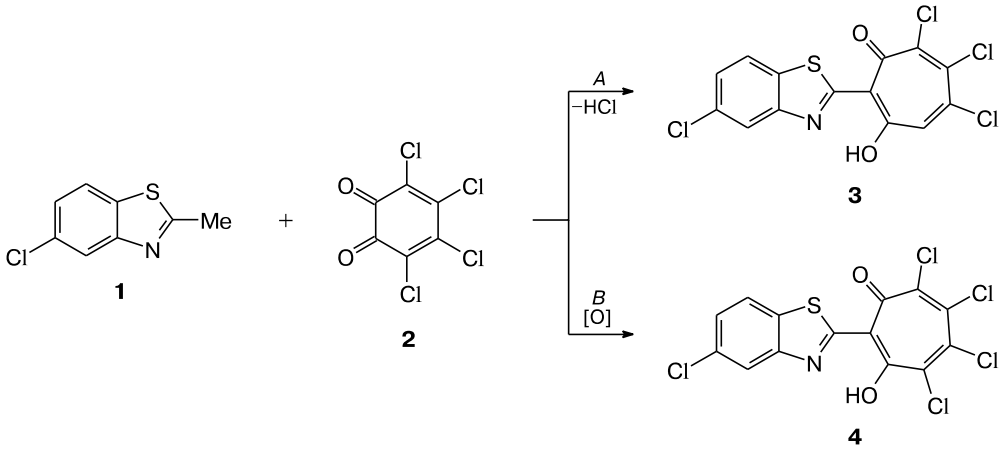
An acid-catalyzed reaction of substituted 5-chloro-2-methylbenzothiazoles with 3,4,5,6-tetrachloro-1,2-benzoquinone leads to 5,6,7-trichloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone and 4,5,6,7-tetrachloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone. Molecular structure of 4,5,6,7-tetrachloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone was established by X-ray crystallography.

Key words: benzothiazoles, *o*-quinones, β-tropolones, intramolecular hydrogen bond, X-ray crystallography.

o-Quinone ring expansion is one of the very promising approaches to the construction of seven-membered tropolone framework. It is known that the reaction proceeds in the series of methylene-active six-membered nitrogen-containing heterocyclic systems (2-methylquinoline[1—3] and 2-methylquinoxaline[4] derivatives), but no data were obtained on the series of five-membered nitrogen-containing heterocycles. In order to study synthetic possibilities of the reaction of *o*-quinone ring expansion, we studied the reaction of 5-chloro-2-methylbenzothiazole (**1**) with 3,4,5,6-tetrachloro-1,2-benzoquinone **2** (Scheme 1). We found that formation of the tropolone framework by the reaction of 5-chloro-2-methylbenzothiazole with 3,4,5,6-tetrachloro-1,2-benzoquinone depends on the re-

Scheme 1



Reagents and conditions: *A*: dioxane, 102 °C; *B*: AcOH, 15—20 °C.

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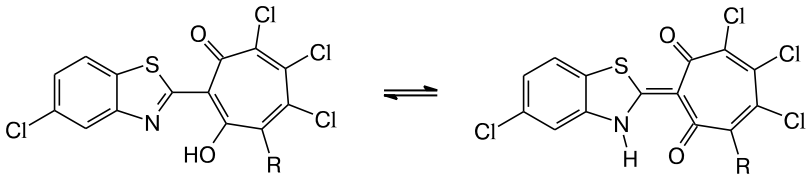
Scheme 2



3(OH), **4**(OH) **3**(NH), **4**(NH)

R = H (**3**), Cl (**4**)

action conditions. Reflux of the starting reactants in dioxane (method *A*) leads to 5,6,7-trichloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone (**3**) in 31% yield, at the same time, a prolonged keeping of compounds **1** and **2** in acetic acid at room temperature (method *B*) gives 4,5,6,7-tetrachloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone (**4**) in low yield (11%).

The mechanism of *o*-quinone ring expansion is described in the literature.[1,2] Formation of 1,3-tropolone by method *A* is accompanied by dehydrochlorination. For the tropolone ring to be formed by method *B*, a twofold excess of the starting quinone is required. The optimum reaction temperature for method *B* is 15—20 °C, and elevation of the temperature of the acetic acid solution of starting reactants (method *B*) results in accumulation of compound **3** in the reaction mixture, as well as side reaction products, whose structures are not yet established. It can be suggested that formation of 1,3-tropolone **3** is controlled by kinetic factors.

The structures of obtained compounds **3** and **4** were confirmed by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectra of compounds **3** and **4** are specifically characterized by the signal for the proton of the tropolone ring in compound **3**, which resonates in the region δ 7.3. The ^{1}H NMR spectra of compounds **3** and **4** also exhibit signal for the proton of the hydroxy group, which resonates in the low-field region δ 14—15 as a broad singlet, indicating the presence of the intramolecular hydrogen bond N···H···O. At the same time, this bond is less strong than in 2-(quinolin-2-yl)-1,3-tropolones, whose signals for the protons of the OH group resonate in the region δ 17—19.[2]

A rapid O—H···N exchange is observed in solutions of compounds **3** and **4**, which is indicated by the broadening of the signal for the proton of the hydroxy group in the ^{1}H NMR spectrum, with the forms **3**(OH), **4**(OH) and **3**(NH), **4**(NH) being in the dynamic equilibrium (Scheme 2). A large contribution of the amino enone form in the solution of compound **4**(NH) is confirmed by the presence of degenerate signals for the carbon atoms (δ 116.2, 124.2, and 125.6) of the tropolone ring in the ^{13}C NMR spectra (DMSO-d_6). Due to the low solubility of compound **3**, its ^{13}C NMR spectrum (DMSO-d_6) was not recorded. The detailed studies of tautomeric equilibrium of compounds **3** and **4** and their energy characteristics depending on the solvent polarity will be performed later using quantum chemical calculations.

Molecular structure of β-tropolone **4** was established by X-ray crystallography, which shows that in the crystal phase tropolone **4** exists as an amino enone form **4**(NH) (Fig. 1).

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts are given relatively to the Me_4Si signal (internal standard). IR spectra of the samples were recorded on a Varian 3100FT-IR Excalibur Series spectrometer using the method of frustrated total internal reflection (FTIR). Chromatography was performed on columns with Al_2O_3 of II—III degree of Brockmann activity. Melting points were measured in glass capillaries on a PTP instrument and were not corrected.

5,6,7-Trichloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone (3). A solution of 5-chloro-2-methylbenzothiazole (**1**) (0.55 g, 3 mmol) and 3,4,5,6-tetrachloro-1,2-benzoquinone (**2**) (0.74 g, 3 mmol) in dioxane (5 mL) was refluxed for 2 h. Then, the solution was cooled and a precipitate that formed was filtered off, washed with dioxane (10 mL) and light petroleum (20—30 mL), dried, and recrystallized from benzene. Compound **3** (0.37 g, 31%) was obtained as bright yellow crystals, m.p. 271—273 °C (benzene). IR, ν/cm^{-1}: 3090, 3050, 2360, 2330, 1555 (C=O), 1491, 1426, 1112, 1071, 949, 890, 813, 762, 598, 575. ^{1}H NMR (DMSO-d_6), δ: 7.30 (s, 1 H, H(4)); 7.55—7.59 (m, 1 H, H_{Ar}); 8.18—8.24 (m, 1 H, H_{Ar}); 8.35 (s, 1 H, H_{Ar}); 15.00 (br.s, 1 H, OH).

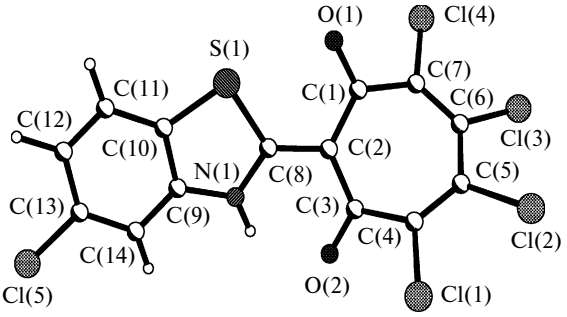


Fig. 1. Molecular structure of 4,5,6,7-tetrachloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone (**4**).

Found (%): C, 42.64; H, 1.16; Cl, 35.92; N, 3.44. $C_{14}H_5Cl_4NO_2S$. Calculated (%): C, 42.78; H, 1.28; Cl, 36.08; N, 3.56.

4,5,6,7-Tetrachloro-2-(5-chlorobenzothiazol-2-yl)-1,3-tropolone (4). A solution of compound **1** (0.92 g, 5 mmol) and compound **2** (2.45 g, 10 mmol) in AcOH (10 mL) was kept at ~20 °C for 100 h. A precipitate that formed was filtered off, dissolved in chloroform, passed through a chromatographic column with silica gel (hexane—CH_2Cl_2 (1 : 5)) collecting the third light yellow fraction to obtain compound **4** (0.18 g). The mother liquor was diluted with water and extracted with chloroform (2×30 mL), the chloroform solution was washed with aqueous soda (3×50 mL) and water (3×50 mL) in a separatory funnel. The chloroform solution was dried with anhydrous Na_2SO_4 for 3—4 h. The solvent was evaporated, the residue was passed through a chromatographic column with silica gel (hexane—CH_2Cl_2 (1 : 5)) collecting the third light yellow fraction to obtain compound **4** (0.05 g). The total yield was 0.23 g (11%), yellow crystals, m.p. 263—265 °C (benzene). IR, ν/cm^{-1}: 3102, 1577, 1548, 1486, 1453, 1420, 1344, 1309, 1283, 1259, 1177, 1117, 1083, 942, 910, 858, 797, 769, 741, 715, 676. ^{1}H NMR (DMSO-d_6), δ: 7.54 ((dd, 1 H, H(6´), J_1 = 10.0 Hz, J_2 = 1.8 Hz); 8.15 (d, 1 H, H(7´), J = 10.0 Hz); 8.30 (s, 1 H, H(4´)); 14.25 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 111.7, 116.2, 124.2, 125.6, 127.3, 130.0, 132.4, 137.2, 139.9, 167.0, 175.5. Found (%): C, 39.18; H, 0.86; Cl, 41.28; N, 3.14. $C_{14}H_4Cl_5NO_2S$. Calculated (%): C, 39.33; H, 0.94; Cl, 41.46; N, 3.28.

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References

1. V. I. Minkin, S. M. Aldoshin, V. N. Komissarov, I. V. Dorogan, Yu. A. Sayapin, V. V. Tkachev, A. G. Starikov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1956 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 2032].
2. Yu. A. Sayapin, B. N. Duong, V. N. Komissarov, I. V. Dorogan, N. I. Makarova, I. O. Bondareva, V. V. Tkachev, G. V. Shilov, S. M. Aldoshin,V. I. Minkin, *Tetrahedron*, 2010, **66**, 8763.
3. Yu. A. Sayapin, V. N. Komissarov, V. I. Minkin, V. V. Tkachev, S. M. Aldoshin, G. V. Shilov, *Zh. Org. Khim.*, 2005, **41**, 1571 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2005, **41**].

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