Brief Communications

Electrocyclic reaction of crown-containing 2-styrylbenzothiazoles

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The photoinduced electrocyclic transformation of 15-crown-5-containing 2-styrylbenzothiazoles into condensed benzothiazoloquinoline derivatives was discovered. The process is accompanied by the formation of a C—N bond and elimination of a hydrogen atom.

Key words: electrocyclic reaction, photocyclization, 2-styrylbenzothiazoles, crown ethers, benzothiazolo[3,2-*a*]quinolines.

It is well known that conjugated diarylethenes (stilbene analogs) undergo photoreversible cyclization to form dihydrophenanthrenes.[1] In the presence of air oxygen, dihydrophenanthrenes are irreversibly oxidized to phenanthrenes, while they can thermally transform into the starting stilbenes in the absence of oxygen.[1—3] For diarylethenes with methyl groups in positions 2 and 6 of the benzene ring, photocyclization is reversible even in the presence of air oxygen.[4,5] When aryl groups are replaced by heterocyclic moieties, *e.g.*, furan or thiophene, the cyclic species become thermally stable and do not return to the open form in the dark.[6—8] The reversible phototransformation of dihetarylethenes into the closed form is used in photochromic lenses, optical memory elements, optoelectronic devices, *etc.*

The photochemical behavior of stilbene analogs, in which one of the phenyl groups is replaced by the heterocycle, does not differ from that of related carbocyclic compounds. They are also characterized by *trans—cis*-isomerization,[9,10] [2+2] photocycloaddition,[11—13] and hexatriene cyclization,[14,15] which affords polycyclic heterocycles after oxidative dehydrogenation. Note that the nitrogen atom in the *ortho*-position to the C=C bond in the starting hetarylphenylethene is not involved in photocyclization: for instance, 2-stilbazole forms benzo[*f*]quinoline.[16]

We have previously shown[17] that oxidative intramolecular cyclization also occurs in the series of 3*H*-indole-based hetarylphenylethenes, including crown-containing compounds. The analysis of published data allowed us to conclude that we pioneered in discovering the electrocyclic reaction in the series of 2-styrylindoles involving the formation of a C—N bond.

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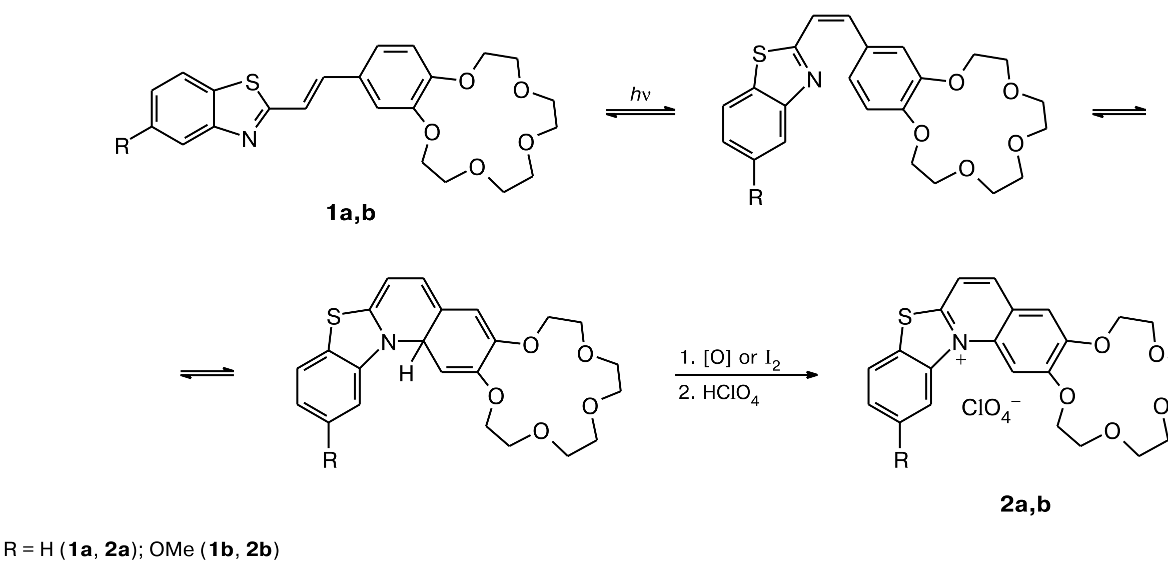
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1290—1292, May, 2005.

Scheme 1



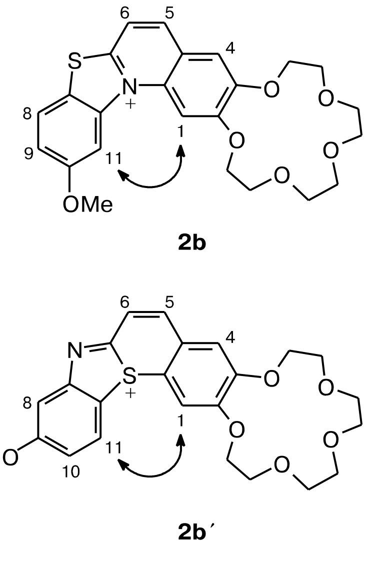
In the present work, we studied the photocyclization of crown-containing 2-styrylbenzothiazoles[18] (CSB) **1**, whose molecules contain a heterocyclic residue and a disubstituted aryl fragment of benzocrown ether at the double bond. Photolysis of these compounds in acetonitrile in the presence of air oxygen produces new compounds **2** (Scheme 1). Signals of aromatic protons in their NMR spectra undergo a substantial downfield shift compared to those of the starting CSB, and the spectra contain no signals of olefinic protons.

Intramolecular cyclization involving both nitrogen and sulfur atoms can be assumed.[19,20] To determine the structure of the product formed, we carried out a detailed analysis of the structure of the heteroaromatic cation formed from CSB **1b**. As can be seen from the data in Scheme 2, the cyclic products are easily discernible from the NOESY spectra due to the methoxy group. In the case of cyclic product **2b**, whose formation involved the nitrogen atom, the spectrum manifests the interaction of two H(1) and H(11) singlets. A cross-peak between the H(1) singlet and H(11) doublet should be observed for the second theoretically possible product **2b**´. As shown in experiment (Fig. 1), the formation of compound **2b** involves the nitrogen atom.

We believe that the discovered reaction proceeds *via* several steps (see Scheme 1). First, the starting compound undergoes *trans—cis*-photoisomerization, and the electrocyclic reaction of CSB affords the 1,2-dihydrobenzothiazoloquinoline, which is oxidized with air oxygen providing the aromatization of the quinoline ring. The reaction is considerably accelerated in the presence of Ag^+ or Hg^{2+} cations as well as iodine.

Thus, we discovered the photoinduced electrocyclic reaction of CSB affording quaternary azonium salts. The new phototransformation of CSB can be considered as a method for the preparation of crown-containing heteroaromatic cations, whose synthesis is difficult to perform by other means.

Scheme 2



Experimental

Melting points were measured on a Mel-Temp II instrument. ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer (working frequency 500.13 MHz) using Me_4Si as internal standard. Chemical shifts were measured with an accuracy of 0.01 ppm, and a measurement error of spin-spin coupling constants was 0.1 Hz. Elemental analyses were carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov

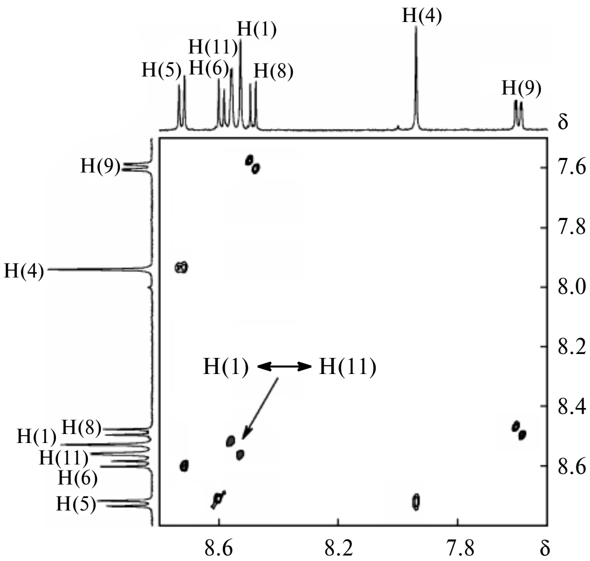


Fig. 1. NOESY spectrum of the product of photochemical cyclization of CSB **1b**.

Institute of Organoelement Compounds (Russian Academy of Sciences, Moscow). The mass spectrum was obtained on a Varian MAT 311A instrument with an ionization energy of 70 eV with direct sample injection into the ionization zone. Electronic absorption spectra were measured on a Specord M-40 spectrophotometer connected to a computer at 20±1 °C. Solutions of CSB were irradiated with the light of a DRK-120 mercury lamp.

2-{(*E*)-2-[3,4-(3,6,9-Trioxaundec-1,11-ylenedioxy)phenyl]ethenyl}-5-methoxy-1,3-benzothiazole (1b) was synthesized similarly to **1a**[18] in 67% yield, m.p. 119—124 °C (from methanol). Found (%): C, 63.11; H, 5.99; N, 3.06. $C_{24}H_{27}NO_6S$. Calculated (%): C, 63.00; H, 5.95; N, 3.06. ^1H ($CDCl_3$), δ: 3.76 (s, 8 H, 4 OCH_2); 3.90 (s, 3 H, OMe); 3.94 (m, 4 H, 2 OCH_2); 4.18 (m, 4 H, 2 $ArOC\underline{H}_2$); 6.88 (d, 1 H, H(5´), *J* = 8.7 Hz); 7.01 and 7.69 (both d, 2 H, H(6), H(7), *J* = 8.7 Hz, *J* = 8.7 Hz); 7.12 (s, 1 H, H(2´)); 7.13 (d, 1 H, H(6´), *J* = 8.7 Hz); 7.22 (d, 1 H, H(a), *J* = 16.2 Hz); 7.44 (d, 1 H, H(b), *J* = 16.2 Hz); 7.47 (s, 1 H, H(4)). Mass spectrum, *m/z* (I_{rel} (%)): 457 $[M]^+$ (94), 456 (38), 368 (16), 326 (33), 325 (52), 324 (100), 310 (13), 299 (16), 298 (26), 240 (13), 127 (24).

Synthesis of cyclization products 2a,b (general procedure). Solutions of *trans*-**1a** or **1b** (0.1 mmol), $AgClO_4$ (0.2 mmol), and I_2 (0.1 mmol) in MeCN (40 mL) were irradiated with the light of a DRK-120 mercury lamp for 16—45 min until **1a** or **1b** was completely consumed (spectrophotometric monitoring). An inorganic precipitate was filtered off, the filtrate was concentrated *in vacuo*, and the residue was recrystallized from methanol.

2,3-(3,6,9-Trioxaundec-1,11-ylenedioxy)[1,3]benzothiazolo[3,2-*a*]quinolin-1a-ium perchlorate (2a). The yield was 42%, m.p. 243—245 °C. Found (%): C, 52.21; H, 4.46; N, 2.30. $C_{23}H_{24}ClNO_9S$. Calculated (%): C, 52.52; H, 4.60; N, 2.66. ^1H NMR, (DMSO-d_6), δ: 3.69 (m, 8 H, 4 OCH_2); 3.90, 3.95 (both m, 2 H each, OCH_2); 4.33, 4.60 (both m, 2 H each, $ArOC\underline{H}_2$); 7.95 (m, 1 H, H(9)); 7.96 (s, 1 H, H(4)); 7.98 (m, 1 H, H(10)); 8.48 (s, 1 H, H(1)); 8.60 (d, 1 H, H(8), *J* = 8.2 Hz); 8.65 (d, 1 H, H(5), *J* = 8.7 Hz); 8.78 (d, 1 H, H(6), *J* = 8.9 Hz); 9.23 (d, 1 H, H(11), *J* = 8.3 Hz).

10-Methoxy-2,3-(3,6,9-trioxaundec-1,11-ylenedioxy)[1,3]benzothiazolo[3,2-*a*]quinolin-1a-ium perchlorate (2b). The yield was 45%, m.p. 236—238 °C. Found (%): C, 51.64; H, 4.33; N, 2.37. $C_{24}H_{26}ClNO_{10}S$. Calculated (%): C, 51.89; H, 4.68; N, 2.52. ^1H NMR (DMSO-d_6), δ: 1.75 (s, 6 H, 2 Me); 4.06 and 4.28 (both s, 6 H, 2 OMe); 7.76 (m, 2 H, H(9), H(10)); 7.97 (s, 1 H, H(4)); 8.02 and 8.78 (both d, 2 H, H(5), H(6), *J* = 6.6 Hz, *J* = 7.9 Hz); 8.31 (s, 1 H, H(1)); 8.39 (d, 1 H, H(8), *J* = 8.5 Hz); 9.08 (d, 1 H, H(11), *J* = 8.4 Hz).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32058, 03-03-32178, and 04-03-32677), CRDF (Grant RC2-2344-MO-02), INTAS (Grant 03-05-4696), and the Ministry of Science and Education of the Russian Federation (Program "Integratsiya").

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*Received October 13, 2004;
in revised form February 21, 2005*