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# Synthesis and Structure of 1-Nitro-4-benzothiazolylsulfanyl- and -sulfonyldienes

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**Abstract**—1-Nitro-4-benzothiazolylsulfanyl- and –sulfonyldienes were synthesized. The former were obtained by thiylation of 1,4-dinitrodienes, and the latter were prepared from the former by oxidation with hydrogen peroxide. The spatial structure of compounds obtained was considered.

Conjugated 1-nitro-4-functionalized systems with activated double bonds are convenient objects for investigation of the trends in the nucleophilic reactions, and also may be used as initial compounds in preparation of new groups of organic compounds [1]. Formerly by an example of 1,4-dinitrodienes **I** we established variable regioselectivity of these reactions depending on the nucleophile character, providing therefore either addition or substitution products, and resulting in the synthesis of versatile polyfunctional alkanes and dienes [3].

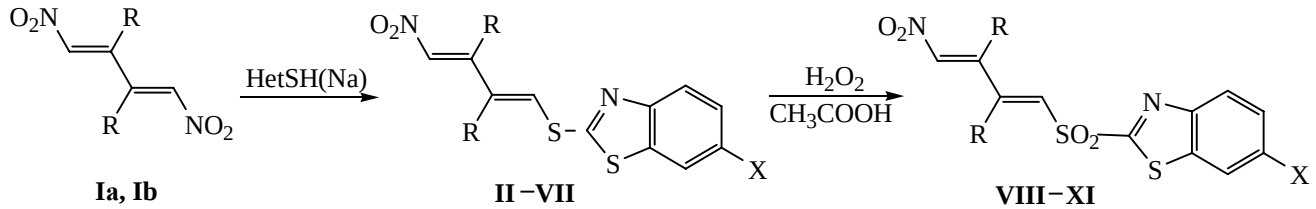
The literature contains rare data on 1-nitro-4-sulfanyl(sulfonyl)diene with aromatic substituents in the sulfur-containing group [2]. A convenient procedure of preparation of 1-nitro-4-arylsulfanyl-dienes was developed consisting in thiylation of the corresponding 1,4-dinitrodienes **I** with thiols or thiolates [2]. In extension of these studies we decided to bring into the thiylation reaction thiols with benzothiazolyl groups that afforded a new series of previously unknown sulfur-containing nitrodienes with a heteryl moiety at sulfur, 1-nitro-4-benzothiazolyl-sulfanyldienes **II–VII**.

The facility of thiylation depends on the structure of the initial 1,4-dinitrodiene. Unsubstituted 1,4-dinitro-1,3-butadiene (**Ia**) reacted with heterylthiols at room temperature in the absence of bases. The reaction of this diene with a less active nucleophile, 5-nitrobenzo-thiazolyl-2-thiol, is an exception for it requires a prolonged heating or an addition of catalytic amount of triethylamine. In less reactive dimethyldiene **Ib** the nitro group suffers substitution only under treatment with thiolate anion.

The oxidation of new 1-nitro-4-benzothiazolylthiodienes **II, V–VII** afforded representatives of another group compounds not described in the literature, 1-nitro-4-benzothiazolylsulfonyldienes **VIII–XI**.

It should be noted that an attempt to oxidize 1-nitro-2-benzothiazolylsulfanylethenes [4] failed, and it was ascribed to the deactivating influence of the acceptor heterocyclic substituent at the sulfur atom [4].

The presence in the heterocyclic moiety of substituents with different electronic effects made it possible to evaluate their influence on the oxidation rate. Inasmuch




**Ia, Ib** **II–VII** **VIII–XI**

R = H (**Ia**): X = H (**II, VIII**), OEt (**III**), $NO_2$ (**IV**); R = $CH_3$ (**Ib**): X = H (**V, IX**), OEt (**VI, X**), $NO_2$ (**VII, XI**).

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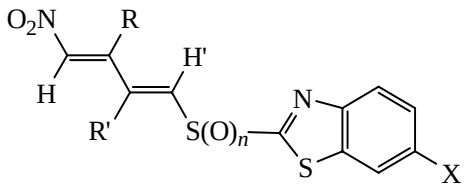
as the reaction occurs owing to the presence of the unshared electron pairs of the sulfide sulfur, firstly, the oxidation under mild conditions should not change the geometry of the compound, and, secondly, the rate of conversion of sulfide into sulfone should be decreased by electron-acceptor substituents and increased by electron-donor ones [5]. The latter suggestion is confirmed by easier oxidation at the presence in the heterocycle of an ethoxy substituent and lower activity of nitrosulfanyldiene **VII** as compared to compound **V** lacking a nitro group in the benzothiazole ring.



The spatial structure of dienes synthesized was derived from the detailed analysis of $^1$H NMR spectra. In the $^1$H NMR spectra of unsubstituted dienes **II–IV**, and **VIII** the two coupling constants of vinyl protons correspond to their *trans*-location ($J_{HR}$13 and $J_{H'R'}$16 Hz for compounds **II** and **III**) indicating the *E,E*-structure of the diene chain. The configuration of 2,3-dimethyl-substituted dienes **V–VII**, **IX–XI** may be deduced from the position of proton signals from the methyl groups. Inasmuch as at the reciprocal *trans*-position of the nitro and methyl groups the chemical shift of protons belonging to the latter does not exceed 1.95 ppm [6], the appearance of signals in the region 2.40–2.50 ppm evidences the *cis*-position of these groups. The shift of the signal from the second methyl group in the spectra of 1-nitro-4-heterylsulfonyl-2,3-dimethylbutadienes **IX–XI** to the region 2.30–2.35 ppm also indicates its cis-position with respect to the electron-acceptor sulfonyl group. Since the oxidation as a rule does not lead to changes in the configuration we may consider that in the initial 1-nitro-4-heterylsulfanyl-2,3- dimethylbutadienes **V–VII** the methyl and sulfanyl groups are also in *cis*-position with respect to each other. Therefore all synthesized 1-nitro-4-heterylsulfanyl(sulfonyl)butadienes were obtained as *E,E*-isomers.

## EXPERIMENTAL

UV spectra were recorded on spectrophotometer SF-2000. $^1$H NMR spectra were registered on spectrometer Bruker-AC 200 (200 MHz), internal reference HMDS. The reaction progress was monitored by TLC on Silufol UV-254 plates, eluent hexane–acetone, 2:1. Dinitrodienes **Ia** and **Ib** were obtained by oxidative bromination of corresponding 1,4-dinitro-2-butenes disodium salts along the known procedure [7].

**General procedure for the synthesis of 4-sulfanyl-1-nitro-1,3-butadienes II–IV**. To a suspension of 1 mmol of benzothiazolyl-2-thiol in 5 ml of anhydrous methanol was added at room temperature a solution of 1 mmol of 1,4-dinitro-1,3-butadiene (**Ia**) in 20 ml of anhydrous methanol. In 2 h the reaction mixture was cooled to 0°C, and the reaction products **II–IV** were filtered off.

**4-(Benzothiazol-2-yl)sulfanyl-1-nitro-1,3-butadiene (II).** Yield 0.084 g (32%), mp 129–130°C (from ethanol). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 280 (12110), 369 (11760). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 6.60 d.d (R'), 7.10 d (H, $J_{HR}$ 13 Hz), 7.30 d (H', $J_{H'R'}$ 16 Hz), 7.77 m (R), 7.38 d, 7.78 m, 7.80 m, 7.95 d (Het). Found, %: C 49.94, 49.95; H 2.76, 2.78; N 10.67, 10.69. $C_{11}H_8N_2O_2S_2$. Calculated, %: C 50.06; H 3.03; N 10.60.

**1-Nitro-4-(5-ethoxybenzothiazol-2-yl)sulfanyl-1,3-butadiene (III).** After separating 0.2 g (48%) of disulfide and subsequent cooling compound **III** was obtained in 0.015 g (5%) yield, mp 93–95°C (from ethanol). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 297 (39850), 377 (37740). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t ($CH_3$), 4.05 q ($CH_2$), 6.58 m (R'), 7.10 d (H, $J_{HR}$ 13 Hz), 7.10 d (H', $J_{H'R'}$ 16 Hz), 7.27, 7.76, 7.84 (Het). Found, %: C 50.18, 50.15; H 3.91, 3.89; N 9.28, 9.30. $C_{13}H_{12}N_2O_3S_2$. Calculated, %: C 50.65; H 3.89; N 9.09.

**1-Nitro-4-(5-nitrobenzothiazol-2-yl)sulfanyl-1,3-butadiene (IV)** was obtained after boiling the reaction mixture for 48 h, yield 0.1 g (33%), mp 155–156°C ($CCl_4$). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 244 (18060), 364 (28130). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 6.66 m (R), 7.16 d (H, $J_{HR}$ 16 Hz), 7.22 d (H', $J_{H'R'}$ 14 Hz), 7.72 m (R), 8.05 d, 8.35 d, 8.75 s (Het). Found, %: C 42.98, 42.97; H 2.73, 2.72; N 13.64, 13.61. $C_{11}H_7N_3O_4S_2$. Calculated, %: C 42.71; H 2.27; N 13.59.

**General procedure for the synthesis of 4-sulfanyl-1-nitro-2,3-dimethyl-1,3-butadienes V–VII.** To a suspension of 3 mmol of dinitrodiene **Ib** in 10 ml of methanol cooled to –5–0°C was added dropwise a solution of sodium thiolate prepared from 0.5 g (3 mmol) of benzothiazolyl-2-thiol in 5 ml of methanol and 0.069 g (3 mmol) of sodium in 3 ml of methanol. After keeping the reaction mixture at 0°C for 40 min the crystalline reaction product was filtered off.

**4-(Benzothiazol-2-yl)sulfanyl-1-nitro-2,3-dimethyl-1,3-butadiene (V).** Yield 0.53 g (60%), mp 126–127°C, 156°C ($CCl_4$). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 244 (36244), 282 (28732), 361 (33951). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (R'), 2.43 s (R), 7.20 d (H'), 7.65 (H), 7.43 d, 7.44 m, 7.94 m, 7.96 d (Het). Found, %: C 53.39, 53.45; H 4.28, 4.27; N 9.70, 9.69. $C_{13}H_{12}N_2O_2S_2$. Calculated, %: C 53.42; H 4.10; N 9.59.

**1-Nitro-4-(5-ethoxybenzothiazol-2-yl)sulfanyl-2,3-dimethyl-1,3-butadiene (VI).** Yield 0.48 g (72%), mp 117–119°C. UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 244, 282, 310 ïλ, 371. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (R'), 2.45 s (R), 7.15 s (H'), 7.60 (H), 1.45 t ($CH_3$), 4.05 q ($CH_2$), 7.05 d, 7.25 s, 7.80 d (Het). Found, %: C 53.46, 53.49; H 4.82, 4.89; N 8.36, 8.30. $C_{15}H_{16}N_2O_3S_2$. Calculated, %: C 53.57; H 4.76; N 8.33.

**1-Nitro-4-(5-nitrobenzothiazol-2-yl)sulfanyl-2,3-dimethyl-1,3-butadiene (VII).** Yield 0.24 g (72%), mp 135–137°C. UV spectrum (DMCO), $\lambda_{max}$, nm (ε): 368 (22400). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.03 s (R'), 2.40 s (R), 7.09 s (H), 7.39 m (H'), 7.95 d, 8.22 d, 8.59 s (Het). Found, %: C 46.24, 46.29; H 3.38, 3.39; N 12.52, 12.50. $C_{13}H_{11}N_3O_4S_2$. Calculated, %: C 46.29; H 3.26; N 12.46.

**General procedure for the synthesis of 4-sulfonyl-1-nitro-1,3-butadienes VIII–XI.** To a suspension of 0.4 mmol of 4-sulfanyl-1-nitro-1,3-butadienes **II, V–VII** in 5 ml of glacial acetic acid at room temperature (**VIII**) or at boiling (**IX–XII**) was added by portions 10 ml of 30% hydrogen peroxide solution. On cooling the pale yellow crystals of compounds **VIII–XI** were filtered off.

**4-(Benzothiazol-2-yl)sulfonyl-1-nitro-1,3-butadiene (VIII)**. After keeping the reaction mixture for 5 days compound **VIII** was isolated in 0.045 (38%) yield, mp 178°C (decomp., from ethanol). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 279 (17880), 298 (17930). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.20 (R'), 7.28 (H, $J_{HR}$ 15 Hz), 7.40 (H', $J_{H'R'}$ 14 Hz), 7.64 (R), 7.60–7.65 m, 8.10 m, 8.25 d (Het). Found, %: C 44.89; H 2.98; N 9.65. $C_{11}H_8N_2O_4S_2$. Calculated, %: C 44.59; H 2.70; N 9.46.

**4-(Benzothiazol-2-yl)sulfonyl-1-nitro-2,3-dimethyl-1,3-butadiene (IX).** After boiling for 2 h compound **IX** was isolated in 0.2 g (63%) yield, mp 155–157°C (metanol). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 282 (17880). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (R'), 2.43 s (R), 6.75 s (H'), 7.15 s (H), 7.55 m, 8.10 m (Het). Found, %: C 48.33, 48.29; H 3.99, 3.97; N 8.80, 8.85. $C_{13}H_{12}N_2O_4S_2$. Calculated, %: C 48.14; H 3.70; N 8.64.

**1-Nitro-4-(5-ethoxybenzothiazol-2-yl)sulfonyl-2,3-dimethyl-1,3-butadiene (X).** After boiling for 10 min compound **X** was isolated in 0.13 g (34%) yield, mp 91–93°C (from ethanol). UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (ε): 261 (23070), 323 (19880). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (R'), 2.45 s (R), 6.75 s (H'), 7.12 s (H), 1.50 t ($CH_3$), 4.15 q ($CH_2$), 7.20–7.40 m, 8.10 d (Het). Found, %: C 48.48, 48.54; H 4.85, 4.82; N 7.88, 7.80. $C_{15}H_{16}N_2O_5S_2$. Calculated, %: C 48.91; H 4.35; N 7.61.

**1-Nitro-4-(5-nitrobenzothiazol-2-yl)sulfonyl-2,3-dimethyl-1,3-butadiene (XI).** After boiling for **a** week compound **XI** was isolated in 0.02 g (15%) yield, mp 105°C (decomp., from ethanol). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (R'), 2.50 s (R), 7.00 s (H'), 7.50 s (H), 8.25 d, 8.50 d, 9.30 s (Het). Found, %: C 42.34, 42.36; H 3.10, 3.03; N 11.84, 11.80. $C_{13}H_{11}N_3O_6S_2$. Calculated, %: C 42.74; H 3.01; N 11.51.

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