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DINITROSULFODIENES OF THE THIOLENE 1,1-DIOXIDE SERIES IN ELECTRON-TRANSFER REACTIONS

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Conjugated aliphatic 1,4-dinitrodiene structures are active oxidants, and in the presence of 2 equivalents of an electron donor (Na/Hg, $C_{10}H_8^{2-}2K^+$, KI) are converted to stable dinitro anions [1, 2]. The structure of dinitro dienes of the thiolene 1,1-dioxide series [3, 4] of the **1a-d** type is characterized by the fact that their diene system is constructed from endocyclic and exocyclic conjugated multiple bonds of a five-membered heterocycle, and the molecule has an additional electron-acceptor substituent: the SO_2 group, which affects the characteristic features of reactions with electron donors.

In contrast to open-chain analogs, dinitrosulfodienes **1a,c** react *via* an electron-transfer route with such representatives of donor reagents as N,N-dimethylaniline. These reactions are carried out at room temperature in alcoholic solution, and lead to formation of stable crystalline molecular complexes **2a,b** in which the role of the donor component is played by N,N-dimethylaniline and the role of the acceptor component is played by the electron-deficient structure of the heterocyclic dinitrosulfodiene. Evidence that **4a,b** are complex compounds comes from the presence in their electronic spectra of a charge-transfer band at λ_{max} ~450 nm (ε 2000-4000), close to the position of such a band (λ_{max} 443 nm, ε ~33000) in molecular complexes formed by 3-methyl-2,4-dinitrothiophene dioxide and pyridine [5, 6]. The binary composition of complexes **2a,b** is also confirmed by ^{1}H NMR spectra and elemental analysis.

In the presence of MeONa dinitrosulfodienes **1a-d**, like the linear analogs [1, 2], are converted to disodium salts **3a-d** which are stable in solutions and unstable in the crystalline state. Formation of salts **3a-d** is confirmed by electronic spectra taken in 0.1 N NaOH solution, in which the bands at λ_1 310-320 (ε 6000-16000) and λ_2 360 nm (ε 2500-8600) correspond to the conjugated dinitro anions.

As preparative proof of the structure, the salts **3a-d** were subjected to oxidation and protonation under conditions described earlier for conjugated dinitronates [2, 7]. Thus bromine treatment of a solution of nitronate **3a** in absolute MeOH at room temperature leads to formation of dinitrosulfodiene **1a**, and when a solution of salt **3a** is acidified with AcOH or HCl, the 3-methyl-4-nitro-2-(α-nitrobenzyl)-2-thiolene-1,1-dioxide (**4**) is isolated.

The starting 3-methyl-4-nitro-2-(1-nitro-1-arylmethylene) 3-thiolene-1,1-dioxides **1a-d** were synthesized by the procedure in [4].

3-Methyl-4-nitro-2-(α-nitrobenzyl)-2-thiolene 1,1-Dioxide (4). Mp 189-191°C (MeOH). Mass spectrum, *m*/*z* 312 $[M]^+$. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 2.00 (3H, s, CH_3); 3.92-4.30 (2H, m, $^2J_{AB}$ = 15, CH_2); 5.30 (1H, s, CH); 5.63 (1H, m, $^3J_{AX}$ = 6, $^3J_{BX}$ = 2, $C_{(4)}HNO_2$); 7.52, 7.91 (5H, m, CH arom.). IR

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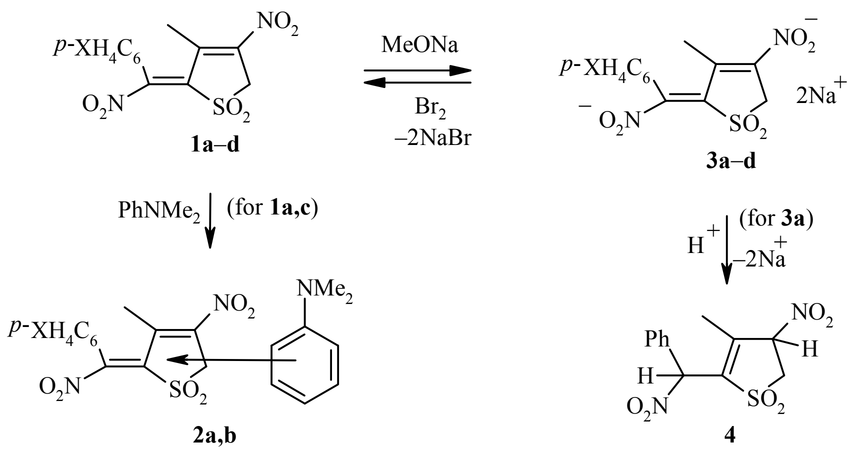

1a, 2a, 3 X = H, **1b, 3b** R = Me, **1c, 2b, 3c** R = Cl, **1d, 3d** R = NO_2

spectrum (nujol), λ, cm^{-1}: 1620 (C=C, Ar); 1570, 1350 (NO_2), 1350, 1140 (SO_2). Found, %: C 46.28, 46.31; H 3.49, 3.50; N 9.24, 9.28. $C_{12}H_{12}N_2O_6S$. Calculated, %: C 46.15; H 3.85; N 8.97. M 312.

Molecular Complex of 3-Methyl-4-nitro-2-(α-nitrobenzylidene)-3-thiolene 1,1-Dioxide with N,N-Dimethylaniline (3a). Mp 299-300°C (with decomposition). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.90 (3H, s, CH_3); 3.00 (6H, s, $N(CH_3)_2$); 4.50 (2H, s, CH_2); 6.60, 6.80, 7.40, 7.55, 7.68, 7.75 (10H, m, CH arom.). Found, %: C 55.58, 55.57; H 4.74, 4.78; N 9.92, 9.66. $C_{20}H_{21}N_3O_6S$. Calculated, %: C 55.68; H 4.87; N 9.74.

Molecular Complex of 3-Methyl-4-nitro-2-[α-nitro-1-(*p*-chlorophenyl)methylene]-3-thiolene 1,1-Dioxide with N,N-Dimethylaniline (3b). Mp 297-299°C (with decomposition). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.95 (3H, s, CH_3); 3.00 (6H, s, $N(CH_3)_2$); 4.55 (2H, s, CH_2); 6.65, 6.80, 7.45, 7.50, 7.70, 7.80 (9H, m, CH arom.). Found, %: N 9.00, 9.02. $C_{20}H_{20}ClN_3O_6S$. Calculated, %: N 9.02.

REFERENCES

1. E. S. Lipina and V. V. Perekalin, *Acta Phys. Chem.*, **19**, 125 (1973).
2. E. S. Lipina and V. V. Perekalin, *Zh. Obshch. Khim.*, **34**, 3644 (1965).
3. I. E. Efremova, S. V. Bortnikov, and V. M. Berestovitskaya, *Zh. Obshch. Khim.*, **71**, 1047 (2001).
4. V. M. Berestovitskaya, I. E. Efremova, S. V. Bortnikov, I. A. Litvinov, and O. N. Kataeva, *Zh. Obshch. Khim.*, **72**, 2035 (2002).
5. V. M. Berestovitskaya, I. E. Efremova, A. L. Khlytin, G. A. Berkova, V. P. Pozdnyakov, and D. A. Gamazin, *Zh. Org. Khim.*, **32**, 152 (1996).
6. I. E. Efremova, L. V. Lapshina, and V. M. Berestovitskaya, *Izv. RGPU, Estestvennye i Tochnye Nauki*, No. 2 (4), 104 (2002).
7. V. M. Berestovitskaya, M. V. Titova, and V. V. Perekalin, *Zh. Org. Khim.*, **18**, 1783 (1982).