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LETTERS TO THE EDITOR

HALOGENATION OF 2-ARYLIDENE-3-METHYL-4-NITRO-3-THIOLENE-1,1-DIOXIDES

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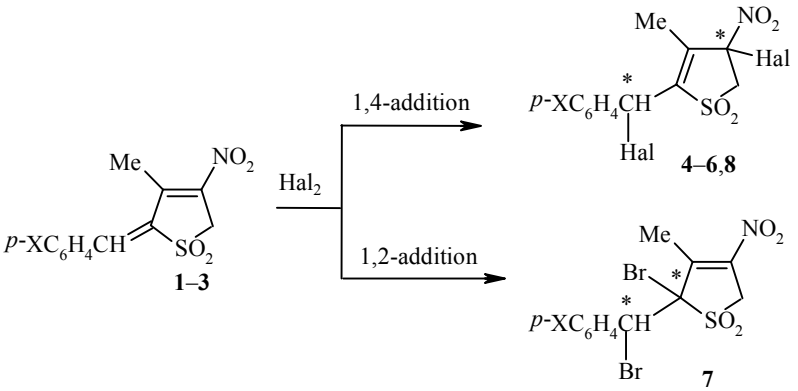
Introduction of halogen atoms onto the ring of nitrothiolene-1,1-dioxide and its derivatives opens up a synthesis route for novel types of functionalized heterocyclenes [1,2]. 2-Arylidene-3-methyl-4-nitro-3-thiolene-1,1-dioxides **1-3** [3,4], whose molecules contain an s-*trans* fixed diene system activated by two electron-acceptor functional groups (NO_2 and SO_2), are convenient systems for constructing original groups of halogen derivatives of nitrothiolene-1,1-dioxides.

We have carried out for the first time the halogenation of 2-arylidene-3-methyl-4-nitro-3-thiolene-1,1-dioxides. Boiling compounds **1-3** with excess bromine (1:5) in chloroform solution for 14 h leads to synthesis of 1,4-addition products **4-6** as mixtures of diastereomers. In the case of *p*-nitrobenzylidene-substituted **3**, the ^{1}H NMR spectrum in addition detects the stereochemically homogeneous 1,2-addition product **7**.



1 X = H, **2** X = Cl, **3** X = NO_2; **4** Hal =Br, X = H; **5** Cl; **6**,**7** NO_2; **8** Hal = Cl, X = NO_2

Compound **3** was chlorinated in acetic acid in the presence of HBr for 24 h. The dichloride **8** was isolated as a result, which according to the ^{1}H NMR spectrum is stereochemically homogeneous.

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The starting 2-arylidene-3-methyl-4-nitro-3-thiolene-1,1-dioxides **1,3** were synthesized according to the procedures in [4]; 3-methyl-4-nitro-2-*p*-chlorobenzylidene-3-thiolene-1,1-dioxide (**2**) was obtained for the first time.

2-*p*-Chlorobenzylidene-3-methyl-4-nitro-3-thiolene-1,1-dioxide (2). Mp 194-195°C (ethanol). ^{1}H NMR spectrum (CD_3CN), δ, ppm, *J* (Hz): 2.4 (3H, t, *J* = 1.7, CH_3); 4.32 (2H, q, *J* = 1.7, CH_2); 7.06 (1H, s, CH); 7.6 (4H, m, Ar). IR spectrum (KBr), ν, cm^{-1}: 1555, 1340 (NO_2); 1330, 1120 (SO_2). Found, %: C 48.09; H 3.45; N 4.71. $C_{12}H_{10}ClNO_4S$. Calculated, %: C 48.08; H 3.34; N 4.67.

4-Bromo-2-(1'-bromo-1'-phenyl)methyl-3-methyl-4-nitro-2-thiolene-1,1-dioxide (4) (as a mixture of diastereomers in 20:1 ratio). Mp 108-110°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 1.95, 2.2 (3H, s, CH_3); 4.15, 4.55 (2H, q, *J* = 15, CH_2); 6.10, 6.05 (1H, s, CH); 7.35, 7.55 (5H, m, Ar). IR spectrum (KBr), ν, cm^{-1}: 1580, 1340 (NO_2); 1340, 1160 (SO_2). Found, %: C 33.99; H 2.76, N 3.48. $C_{12}H_{11}Br_2NO_4S$. Calculated, %: C 33.88; H 2.59; N 3.29.

4-Bromo-2-(1'-bromo-1'-*p*-chlorophenyl)methyl-3-methyl-4-nitro-2-thiolene-1,1-dioxide (5) (as a mixture of diastereomers in 10:1 ratio). Mp 125-130°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 1.95, 2.20 (3H, s, CH_3); 4.15, 4.50 (2H, q, *J* = 15, CH_2); 6.05, 6.00 (1H, s, CH); 7.35, 7.45 (5H, m, Ar). IR spectrum (KBr), ν, cm^{-1}: 1570, 1325 (NO_2); 1320, 1145 (SO_2). Found, %: C 31.20; H 2.16; N 3.04. $C_{12}H_{10}Br_2ClNO_4S$. Calculated, %: C 31.36; H 2.18; N 3.05.

4-Bromo-2-(1'-bromo-1'-*p*-nitrophenyl)methyl-3-methyl-4-nitro-2-thiolene-1,1-dioxide (6), 2-Bromo-2-(1'-bromo-1'-*p*-nitrophenyl)methyl-3-methyl-4-nitro-3-thiolene-1,1-dioxide (7) (identified in a mixture in 3:4 ratio). Mp 135-138°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): for compound **6** (as a mixture of diastereomers in 20:1 ratio); 2.00, 2.10 (3H, s, CH_3); 4.15, 4.45 (2H, q, *J* = 15, CH_2); 6.10, (1H, s, CH); 7.78, 8.30 (4H, m, Ar); for compound **7**: 2.20 (3H, s, CH_3); 4.45 (2H, s, CH_2); 6.05 (1H, s, CH); 7.78, 8.30 (4H, m, Ar). IR spectrum (KBr), ν, cm^{-1}: 1565, 1355 (NO_2); 1330, 1150 (SO_2). Found, %: C 30.83; H 2.21; N 5.84. $C_{12}H_{10}Br_2N_2O_6S$. Calculated, %: C 30.66; H 2.13; N 5.96.

4-Chloro-2-(1'-chloro-1'-*p*-nitrophenyl)methyl-3-methyl-4-nitro-2-thiolene-1,1-dioxide (8). Mp 149-150°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 2.00 (3H, s, CH_3); 4.05, 4.50 (2H, q, *J* = 15, CH_2); 6.07 (1H, s, CH); 7.78, 8.35 (4H, m, Ar). IR spectrum (KBr), ν, cm^{-1}: 1570, 1325 (NO_2); 1320, 1140 (SO_2). Found, %: C 37.73; H 2.80; N 4.47. $C_{12}H_{10}Cl_2N_2O_6S$. Calculated, %: C 37.80; H 2.62; N 7.35.

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