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# Synthesis of 3-aryl-5,7-dinitrothiochromane 1,1-dioxides based on 2,4,6-trinitrotoluene

**Mikhail D. Dutov, Ol'ga V. Serushkina and Svyatoslav A. Shevelev***

*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.*
*Fax: +7 095 135 5328; e-mail: shevelev@mail.ioc.ac.ru*

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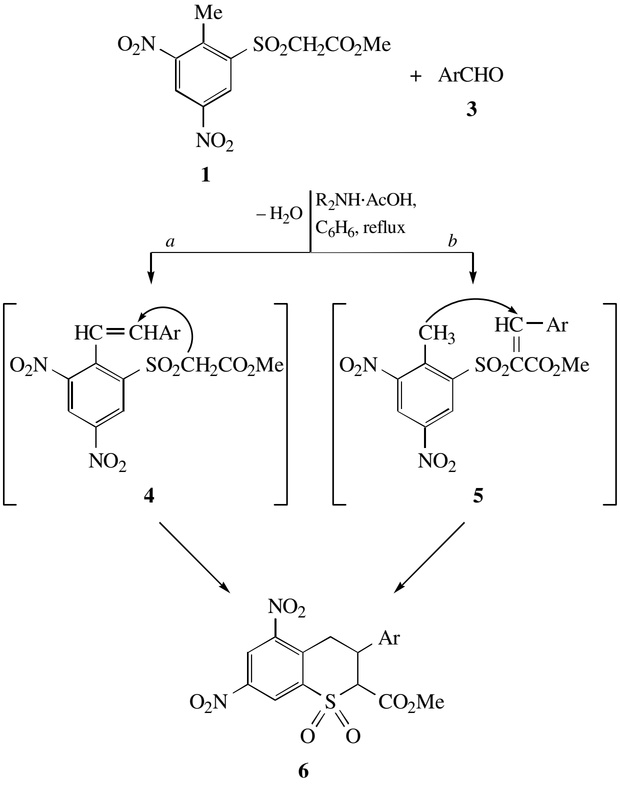
3-Aryl-5,7-dinitrothiochromane 1,1-dioxides are formed by the condensation of methyl (2-methyl-3,5-dinitrobenzenesulfonyl)acetate and ethyl (2-methyl-3,5-dinitrobenzenesulfonyl)propionate, which are the products of 2,4,6-trinitrotoluene transformations, with aromatic aldehydes under conditions of the Knoevenagel reaction.

This study was performed in the context of the chemical utilization of 2,4,6-trinitrotoluene (TNT)[1] to prepare multipurpose intermediates for the synthesis of polyfunctional heterocyclic compounds.

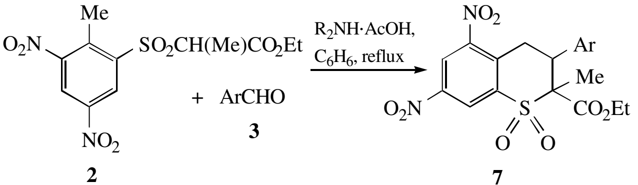
We examined the reactions of sulfone **1**, which was synthesised previously[2] from TNT, with aromatic aldehydes under conditions of the Knoevenagel reaction. The equimolar amounts of the sulfone and ArCHO in benzene in the presence of secondary aliphatic amine acetates were heated with the continuous removal of water formed in the reaction (Scheme 1).

Under these conditions, 3-aryl-5,7-dinitrothiochromane 1,1-dioxide **6** was the reaction product. It can be formed either by the initial formation of stilbene **4** in the condensation of ArCHO **3** with the methyl group of sulfone **1** followed by the addition of an active methylene unit at the double bond of stilbene **4** (pathway *a*) or by the condensation of aldehydes **3** with the active methylene unit of sulfone **1** to form arylidene **5** followed by the intramolecular addition of an active methyl group at the double bond of arylidene **5** (pathway *b*).



**a** Ar = Ph
**b** Ar = 4-MeOC$_6$H$_4$
**c** Ar = 4-Me$_2$NC$_6$H$_4$
**d** Ar = 4-ClC$_6$H$_4$
**e** Ar = 4-FC$_6$H$_4$
**f** Ar = 4-NO$_2$C$_6$H$_4$
**g** Ar = 3-pyridyl

**Scheme 1**



**b** Ar = 4-MeOC$_6$H$_4$
**e** Ar = 4-FC$_6$H$_4$
**g** Ar = 3-pyridyl

**Scheme 2**

It is likely that the reaction can simultaneously proceed *via* pathways *a* and *b*. At least, the feasibility of pathway *a* was demonstrated by the formation of 3-aryl-2-methyl-5,7-dinitrothiochromane 1,1-dioxides **7** with the use of sulfone **2**[2] in this reaction (Scheme 2).

Thus, we developed a general procedure[†] for preparing previously unknown 3-aryl-5,7-dinitrothiochromane 1,1-dioxides **6** and **7**. Compounds **6** and **7** were identified by $^1$H NMR spectroscopy and elemental analysis.[‡] The stereochemistry of these compounds will be published elsewhere.

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[†] *General procedure.* Piperidine (0.1 ml) and glacial acetic acid (0.11 ml) were added to a mixture of 0.01 mol of sulfone **1** or **2** and 0.011 mol of ArCHO in 30 ml of benzene. The mixture was refluxed for 2–5 h (with TLC monitoring) with the use of a Dean–Stark trap to remove water and then cooled. The precipitated product was filtered off, washed with a dilute aqueous NaCl solution, dried in air, and recrystallised from an acetone–methanol mixture.

[‡] The $^1$H NMR spectra (in [$^2$H$_6$]acetone) were measured on a Bruker AC-200 instrument.

**6a**: 53% yield, mp 217–219 °C. $^1$H NMR, $\delta$: 9.02 (d, 1H, $^4J$ 2.0 Hz), 8.90 (d, 1H, $^4J$ 2.0 Hz), 7.31–7.48 (m, 5H), 5.17 (d, 1H, $^3J$ 11.0 Hz), 4.07–4.20 (m, 1H), 3.56–3.75 (m, 5H). Found (%): C, 50.44; H, 3.29; S, 8.11; N, 7.02. Calc. for $C_{17}H_{14}N_2O_8S$ (%): C, 50.25; H, 3.47; S, 7.89; N, 6.89.

**6b**: 82% yield, mp 197–199 °C. $^1$H NMR, $\delta$: 9.03 (d, 1H, $^4J$ 2.2 Hz), 8.89 (d, 1H, $^4J$ 2.2 Hz), 7.38 (d, 2H, $^3J$ 8.6 Hz), 6.95 (d, 2H, $^3J$ 8.6 Hz), 5.16 (d, 1H, $^3J$ 11.1 Hz), 4.00–4.15 (m, 1H), 3.75–3.85 (m, 8H). Found (%): C, 49.83; H, 4.00; S, 7.47; N, 6.15. Calc. for $C_{18}H_{16}N_2O_9S$ (%): C, 49.54; H, 3.70; S, 7.35; N, 6.42.

**6c**: 35% yield, mp 185–187 °C. $^1$H NMR, $\delta$: 9.03 (d, 1H, $^4J$ 2.0 Hz), 8.89 (d, 1H, $^4J$ 2.0 Hz), 7.28 (d, 2H, $^3J$ 8.5 Hz), 6.72 (d, 2H, $^3J$ 8.5 Hz), 5.02 (d, 1H, $^3J$ 11.0 Hz), 3.90–4.05 (m, 1H), 3.60–3.72 (m, 5H), 2.94 (s, 6H). Found (%): C, 51.03; H, 4.37; S, 7.23; N, 9.07. Calc. for $C_{19}H_{19}N_3O_8S$ (%): C, 50.78; H, 4.26; S, 7.13; N, 9.35.

**6d**: 24% yield, mp 234–236 °C. $^1$H NMR, $\delta$: 9.05 (d, 1H, $^4J$ 2.1 Hz), 8.91 (d, 1H, $^4J$ 2.1 Hz), 7.52 (d, 2H, $^3J$ 8.9 Hz), 7.44 (d, 2H, $^3J$ 8.9 Hz), 5.29 (d, 1H, $^3J$ 11.3 Hz), 4.10–4.25 (m, 1H), 3.62–3.78 (m, 5H). Found (%): C, 46.14; H, 3.11; S, 7.05; Cl, 8.42; N, 6.03. Calc. for $C_{17}H_{13}ClN_2O_8S$ (%): C, 46.32; H, 2.97; S, 7.27; Cl, 8.04; N, 6.35.

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**6e**: 68% yield, mp 220–222 °C. $^1$H NMR, $\delta$: 9.04 (d, 1H, $^4J$ 2.0 Hz), 8.90 (d, 1H, $^4J$ 2.0 Hz), 7.45–7.58 (m, 2H), 7.19–7.21 (m, 2H), 5.18 (d, 1H, $^3J$ 10.3 Hz), 4.10–4.25 (m, 1H), 3.61–3.75 (m, 5H). Found (%): C, 48.36; H, 3.01; S, 7.84; N, 6.73. Calc. for $C_{17}H_{13}FN_2O_8S$ (%): C, 48.12; H, 3.09; S, 7.56; N, 6.60.

**6f**: 52% yield, mp 264–266 °C. $^1$H NMR, $\delta$: 9.05 (d, 1H, $^4J$ 2.2 Hz), 8.92 (d, 1H, $^4J$ 2.2 Hz), 8.29 (d, 2H, $^3J$ 8.8 Hz), 7.80 (d, 2H, $^3J$ 8.8 Hz), 5.44 (d, 1H, $^3J$ 11.0 Hz), 4.26–4.45 (m, 1H), 3.70–3.81 (m, 2H), 3.64 (s, 3H). Found (%): C, 45.42; H, 3.10; S, 7.15; N, 9.03. Calc. for $C_{17}H_{13}N_3O_{10}S$ (%): C, 45.24; H, 2.90; S, 7.10; N, 9.31.

**6g**: 55% yield, mp 183–185 °C. $^1$H NMR, $\delta$: 9.04 (d, 1H, $^4J$ 2.1 Hz), 8.91 (d, 1H, $^4J$ 2.1 Hz), 8.67 (m, 1H), 8.55 (m, 1H), 7.93 (m, 1H), 7.41 (m, 1H), 5.36 (d, 1H, $^3J$ 11.0 Hz), 4.12–4.30 (m, 1H), 3.70–3.80 (m, 2H), 3.63 (s, 3H). Found (%): C, 47.48; H, 3.14; S, 8.13; N, 10.04. Calc. for $C_{16}H_{13}N_3O_8S$ (%): C, 47.18; H, 3.22; S, 7.87; N, 10.32.

**7b**: 53% yield, mp 145.5–147.5 °C. $^1$H NMR, $\delta$: 9.05 (d, 1H, $^4J$ 2.3 Hz), 8.90 (d, 1H, $^4J$ 2.3 Hz), 7.32 (d, 2H, $^3J$ 8.8 Hz), 6.95 (d, 2H, $^3J$ 8.8 Hz), 4.41–4.49 (m, 1H), 4.08–4.22 (m, 2H), 3.74–3.83 (m, 5H), 1.58 (s, 3H), 1.16 (t, 3H, $^3J$ 7.1 Hz). Found (%): C, 52.01; H, 4.32; S, 7.24; N, 5.88. Calc. for $C_{20}H_{20}N_2O_9S$ (%): C, 51.72; H, 4.34; S, 6.90; N, 6.03.

**7e**: 40% yield, mp 149–151 °C. $^1$H NMR, $\delta$: 9.06 (d, 1H, $^4J$ 2.3 Hz), 8.90 (d, 1H, $^4J$ 2.3 Hz), 7.40–7.53 (m, 2H), 7.12–7.22 (m, 2H), 4.47–4.57 (m, 1H), 4.10–4.22 (m, 2H), 3.77–3.87 (m, 2H), 1.60 (s, 3H), 1.15 (t, 3H, $^3J$ 7.2 Hz). Found (%): C, 50.22; H, 3.94; S, 6.93; N, 5.98. Calc. for $C_{19}H_{17}FN_2O_8S$ (%): C, 50.44; H, 3.79; S, 7.09; N, 6.19.

**7g**: 74% yield, mp 177.5–179.5 °C. $^1$H NMR, $\delta$: 9.08 (d, 1H, $^4J$ 2.3 Hz), 8.55–8.62 (m, 2H), 7.94–7.89 (m, 1H), 7.45–7.39 (m, 1H), 4.62–4.57 (m, 1H), 4.19–4.12 (m, 2H), 3.93–3.87 (m, 2H), 1.70 (s, 3H), 1.15 (t, 3H, $^3J$ 7.2 Hz). Found (%): C, 49.91; H, 4.06; S, 7.52; N, 9.47. Calc. for $C_{18}H_{17}N_3O_8S$ (%): C, 49.65; H, 3.94; S, 7.36; N, 9.65.