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Dedicated to Full Member of the Russian Academy of Sciences I.P. Beletskaya on Her Jubilee

Synthesis of Thiochroman 1,1-Dioxide Derivatives on the Basis of 2,4,6-Trinitrotoluene*

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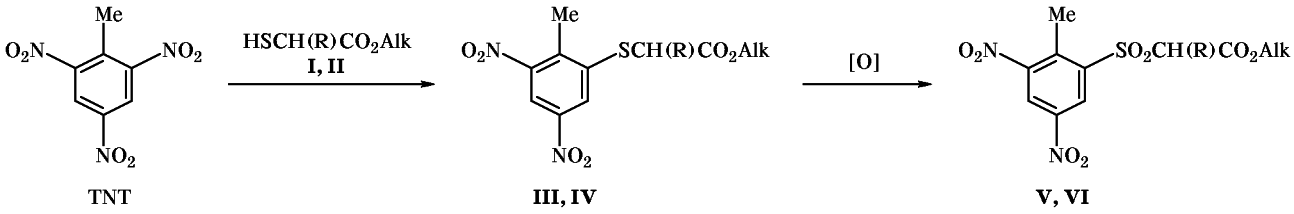
Abstract—Treatment of 2,4,6-trinitrotoluene with β-mercaptocarboxylic acid esters and subsequent oxidation gave 2-(alkoxycarbonyl-R-methylsulfonyl)-4-X-6-nitrotoluenes which were brought into Knoevenagel condensation with aromatic aldehydes (heating in benzene in the presence of secondary amine acetates). As a result of intramolecular cyclization, 2-alkoxycarbonyl-3-aryl-2-R-5-X-7-nitrothiochroman 1,1-dioxides (R = H, Me; X = NO_2, R′SO_2) were obtained. The developed procedure opens the way to hitherto unknown thiochroman 1,1-dioxide derivatives.

The present study was performed in the framework of the program for chemical utilization of an explosive material, 2,4,6-trinitrotoluene (TNT) [2–4]. The program implies transformation of TNT into an accesible starting material for various applications, including the synthesis of polyfunctional fused heterocycles [4] which are difficult or even impossible to obtain by presently known methods.

A usual approach to benzo-fused heterocycles on the basis of TNT involves preliminary transformation of the methyl group and subsequent replacement of the *ortho*-nitro group and intramolecular cyclization [4]. The present communication reports on a different approach to the synthesis of benzo-fused heterocycles on the basis of TNT. As an example, the synthesis of thiochroman 1,1-dioxide derivatives is described. The synthetic scheme includes preliminary transformation of the *ortho*-nitro rather than methyl group and subsequent cyclization by the action of an external reagent.

We previously showed that TNT regioselectively reacts with arene- and alkanethiols in dipolar aprotic solvents in the presence of inorganic bases. Alkyl- or arylthio group replaces mainly or exclusively the *ortho*-nitro group in TNT [5, 6]. In the reaction with mercaptoacetic acid ester (**I**), only the *ortho*-nitro group is replaced [in the presence of K_2CO_3 in *N*-methylpyrrolidinone (NMP) or dimethylformamide (DMF) at 20°C] [5]. The product, sulfide **III** was oxidized to the corresponding sulfone **V** [5]. Likewise,

Scheme 1.



TNT — **III, IV** — **V, VI**

I, **III**, **V**, R = H; **II**, **IV**, **VI**, R = Me; **I**, **V**, Alk = Me; **II**, **VI**, Alk = Et.

* For preliminary communication, see [1].

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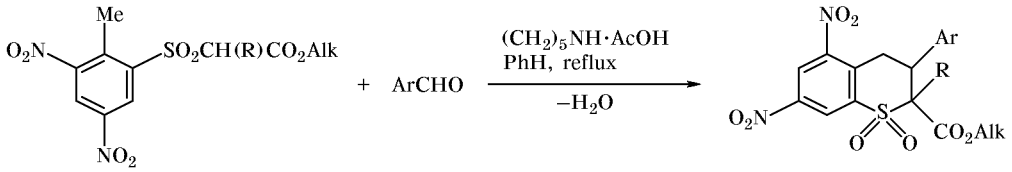
Scheme 2.



V, VI **VII** **VIIIa–VIIIg, IXa–IXc**

V, **VIII**, R = H; **VI**, **IX**, R = Me; **V**, **VIII**, Alk = Me; **VI**, **IX**, Alk = Et; **VIII**, Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-$Me_2NC_6H_4$ (**c**), 4-ClC_6H_4 (**d**), 4-FC_6H_4 (**e**), 4-$O_2NC_6H_4$ (**f**), 3-pyridyl (**g**); **IX**, Ar = 4-$MeOC_6H_4$ (**a**), 4-FC_6H_4 (**b**), 3-pyridyl (**c**).

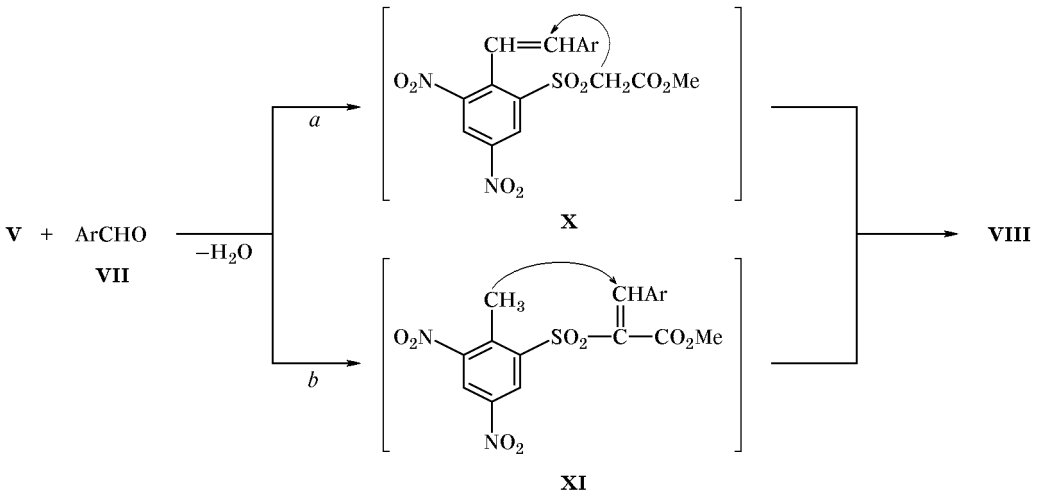
sulfone **VI** was obtained from TNT and ethyl 2-mercaptopropionate (**II**) [5] (Scheme 1).

We examined the reaction of sulfones **V** and **VI** with aromatic aldehydes under conditions of the Knoevenagel condensation: equimolar amounts of **V** or **VI** and aromatic aldehyde ArCHO (**VII**) were heated in benzene in the presence of a catalytic amount of piperidinium acetate (or some other secondary amine acetate) with continuous removal of water released during the reaction. In all cases, the condensation products were derivatives of 5,7-dinitrothiochroman 1,1-dioxide. From sulfone **V**, we obtained 3-aryl-2-methoxycarbonyl-5,7-dinitrothiochroman 1,1-dioxides **VIIIa**–**VIIIg**, and from sulfone **VI**, 3-aryl-2-ethoxycarbonyl-2-methyl-5,7-dinitrothiochroman 1,1-dioxides **IXa**–**IXc** (Scheme 2, Table 1).

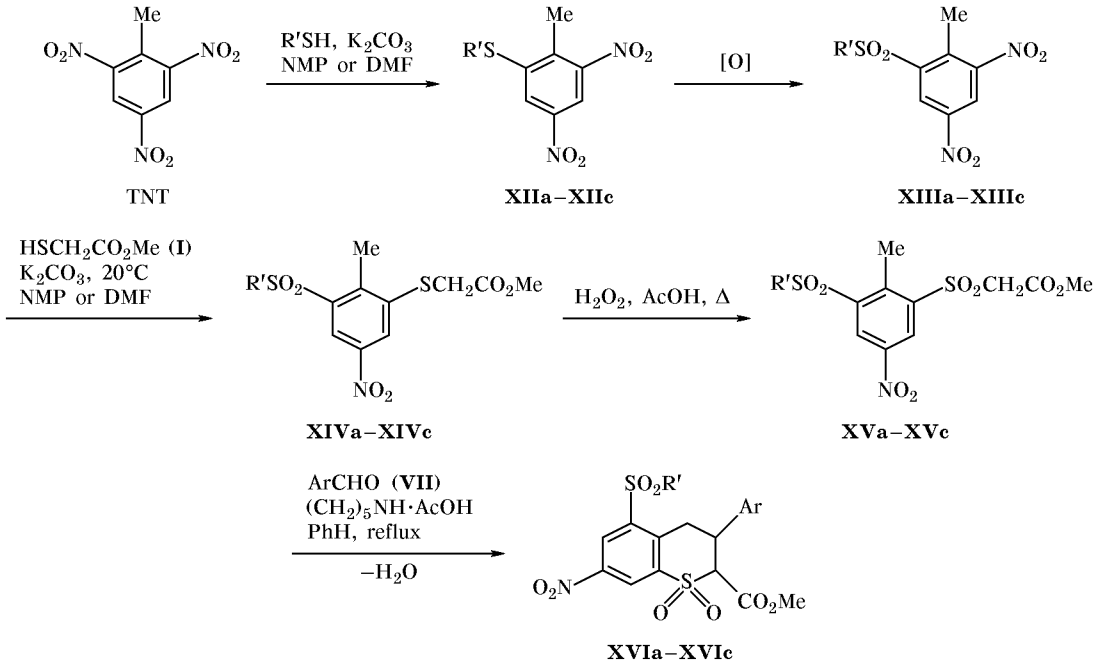
There are two possible ways of formation of thiochroman 1,1-dioxides **VIII** from sulfone **V**. According to pathway *a* (Scheme 3), condensation of aldehyde **VII** at the methyl group of **V** initially gives stilbene **X** which then undergoes intramolecular Michael addition of the active methylene fragment at the double bond. Pathway *b* implies initial condensation of aldehyde **VII** at the active methylene fragment of sulfone **V**, followed by intramolecular attack by the methyl group on the arylmethylene moiety in **XI**. However, in the case of sulfone **VI**, only pathway *a* is possible. Therefore, we presume that in both cases the reaction takes pathway *a*, the more so the reaction conditions for sulfones **V** and **VI** are identical. It should be noted that both 2-R-sulfonyl-4,6-dinitrotoluenes and TNT are known [7, 8] to smoothly react at the methyl group with aromatic aldehydes under analogous conditions (boiling benzene, secondary amine; according to our data, amine acetates also catalyze the reaction) to give the corresponding stilbenes.

We also applied the developed scheme to the synthesis of thiochroman 1,1-dioxides having only one nitro group. For this purpose, we have prepared TNT analogs containing a strongly electron-acceptor sulfonyl group instead of one *orhto*-nitro group: 2-R′-sulfonyl-4,6-dinitrotoluenes **XIIIa**–**XIIIc** [4, 5] (Scheme 4). Sulfones **XIIIa**–**XIIIc** reacted with methyl mercaptoacetate in *N*-methylpyrrolidine or DMF in the presence of K_2CO_3 at 20°C. As a result, the second *ortho*-nitro group was replaced by the

Scheme 3.



Scheme 4.



XII–**XV**, R′ = 4-ClC_6H_4 (**a**), $CH_2CH(CH_3)_2$ (**b**), $CH(CH_3)$ (**c**); **XVI**, R′ = 4-ClC_6H_4, Ar = 4-FC_6H_4 (**a**); R′ = $CH_2CH(CH_3)_2$, Ar = 4-FC_6H_4 (**b**); R′ = $CH(CH_3)$, Ar = 4-$MeOC_6H_4$ (**c**).

$SCH_2CO_2CH_3$ fragment. Sulfides **XIV** were oxidized to the corresponding bis-sulfones **XV** by treatment with 35% hydrogen peroxide in acetic acid (Scheme 4, Table 2). Like sulfone **V**, the reaction of bis-sulfones **XV** with aromatic aldehydes under analogous conditions afforded 3-aryl-2-methoxycarbonyl-5-R′-sulfonyl-7-nitrothiochroman 1,1-dioxides **XVIa**–**XVIc** (Scheme 4, Table 1).

Thus we have developed a preparative procedure for the synthesis of previously unknown 5,7-dinitro- and 5-R′-sulfonyl-7-nitrothiochroman 1,1-dioxide derivatives, starting from 2,4,6-trinitrotoluene. The procedure is based on the condensation of aromatic aldehydes with 4,6-dinitro- or 4-nitro-6-R′-sulfonyltoluenes having an $SO_2CH(R)CO_2Alk$ (R = H, Me) fragment in position *2*.

The structure of the newly synthesized compounds was proved by the ^1H NMR spectra (Table 3), electron impact mass spectra (in all cases, the most abundant ion was that formed by loss of methoxy or ethoxy group from the molecular ion of the methyl and ethyl esters, respectively), IR spectra (ν C=O 1740–1720 cm^{-1}; $\nu_{as}NO_2$ 1600–1500 cm^{-1}; $\nu_s NO_2$ 1400–1350 cm^{-1}; $\nu_{as}SO_2$ 1350–1300 cm^{-1}; $\nu_s SO_2$ 1200–1100 cm^{-1}), and elemental analyses (Table 4).

The steric structure of thiochroman 1,1-dioxides was established by ^1H NMR spectroscopy using compound **VIIId** as an example. The orientation of substituents at C^2 and C^3 was determined on the basis of the corresponding coupling constants and the results of NOE experiments. Protons on C^2, C^3, and C^4 give rise to an *AA′MX* spin system and are readily

Table 1. Yields and melting points of 5,7-dinitro- and 5-R′-sulfonyl-7-nitrothiochroman 1,1-dioxide derivatives **VIII**, **IX**, and **XVI**

Comp. no.	Yield,[a] %	mp, °C (solvent)
VIIIa	53	217–219 (acetone–methanol)
VIIIb	82	197–199 (acetone–methanol)
VIIIc	35	185–187 (acetone–methanol)
VIIId	24	234–236 (acetone–methanol)
VIIIe	68	220–222 (acetone–methanol)
VIIIf	52	264–266 (acetone–methanol)
VIIIg	55	183–185 (acetone–methanol)
IXa	53	145.5–147.5 (acetone–methanol)
IXb	40	149–151 (acetone–methanol)
IXc	74	177.5–179.5 (acetone–methanol)
XVIa	49	254–256 (acetone)
XVIb	56	208–210 (CH_3CN)
XVIc	64	240–242 (acetone–methanol)

[a] Isolated pure product.

Table 2. 2-(Methoxycarbonylmethylthio)-4-R′-sulfonyl-6-nitrotoluenes **XIVa**–**XIVc** and 2-(methoxycarbonylmethylsulfonyl)-4-R′-sulfonyl-6-nitrotoluenes **XVa**–**XVc**

Comp. no.	Yield,[a] %	mp, °C (solvent)	Comp. no.	Yield,[a] %	mp, °C (solvent)
XIVa	83	107–108 (methanol)	**XVa**	76	167–168
XIVb	85	102–103 (etanol)	**XVb**	59	125–126
XIVc	71	99–100 (metanol)	**XVc**	57	173–174 (MeCN–H_2O, 3:2)

[a] Isolated pure product.

identified by both their chemical shifts and coupling constants.

The mode of splitting of the 4-H (δ 3.77 ppm) and 4′-H signals (δ 3.71 ppm) indicates that the first of these is equatorial while the second is axial. The coupling constants $^3J_{2,3}$ = 11.3 Hz, $^3J_{3,4\text{-}ax}$ = 11.3 Hz, and $^3J_{3,4\text{-}eq}$ = 4.6 Hz suggests that the 3-H and 2-H protons occupy axial positions; the corresponding signals appear, respectively, as a triplet of doublets at δ 4.18 ppm and a doublet at δ 5.24 ppm. This conclusion is confirmed by the NOESY spectrum which shows no correlation between 2-H and 3-H, in keeping with *trans* arrangement of these protons. In addition, in the NOESY spectrum we observed correlation peaks between the *ortho*-protons of the *p*-chlorophenyl ring (δ 7.52 ppm, d; *m*-H, δ 7.47 ppm, d) and protons on C^2, C^3, and C^{4a}. These data indicate equatorial orientation of the *p*-chlorophenyl group

Table 3. Elemental analyses and ^{1}H NMR spectra of compounds **VIII**, **IX**, and **XII**–**XVI**

Compound no.	Found, %				Formula	Calculated, %			
	C	H	N	S (Cl)		C	H	N	S (Cl)
VIIIa	50.44	3.29	7.02	8.11	$C_{17}H_{14}N_2O_8S$	50.25	3.47	6.89	7.89
VIIIb	49.83	4.00	6.15	7.47	$C_{18}H_{16}N_2O_9S$	49.54	3.70	6.42	7.35
VIIIc	51.03	4.37	9.07	7.23	$C_{19}H_{19}N_3O_8S$	50.78	4.26	9.35	7.13
VIIId	46.14	3.11	6.03	7.05 (8.42)	$C_{17}H_{13}ClN_2O_8S$	46.32	2.97	6.35	7.27 (8.04)
VIIIe	48.36	3.01	6.73	7.84	$C_{17}H_{13}FN_2O_8S$	48.12	3.09	6.60	7.56
VIIIf	45.42	3.10	9.03	7.15	$C_{17}H_{13}N_3O_{10}S$	45.24	2.90	9.31	7.10
VIIIg	47.48	3.14	10.04	8.13	$C_{16}H_{13}N_3O_8S$	47.18	3.22	10.32	7.87
IXa	52.01	4.32	5.88	7.24	$C_{19}H_{20}N_2O_9S$	51.72	4.34	6.03	6.90
IXb	50.22	3.94	5.98	6.93	$C_{19}H_{17}FN_2O_8S$	50.44	3.79	6.19	7.09
IXc	49.91	4.06	9.47	7.52	$C_{18}H_{17}N_3O_8S$	49.65	3.94	9.65	7.36
XVIa	50.25	3.31	3.03	10.92 (6.04)	$C_{23}H_{17}ClFNO_8S_2$	49.87	3.09	2.53	11.58 (6.40)
XVIb	51.03	4.92	3.26	12.06	$C_{21}H_{22}FNO_8S_2$	50.49	4.44	2.80	12.84
XVIc	51.47	5.08	3.16	12.03	$C_{21}H_{23}NO_9S_2$	50.69	4.66	2.82	12.89
XIVa	47.01	3.75	3.69	14.99 (8.11)	$C_{16}H_{14}ClNO_6S_2$	46.21	3.39	3.37	15.42 (8.52)
XIVb	47.24	5.72	4.12	17.07	$C_{14}H_{19}NO_6S_2$	46.52	5.30	3.88	17.74
XIVc	45.38	5.21	4.35	17.90	$C_{13}H_{17}NO_6S_2$	44.94	4.93	4.03	18.46
XVa	43.55	3.71	3.67	13.80 (7.54)	$C_{16}H_{14}ClNO_8S_2$	42.91	3.15	3.13	14.32 (7.92)
XVb	43.08	5.15	4.02	15.86	$C_{14}H_{19}NO_8S_2$	42.74	4.87	3.56	16.30
XVc	41.57	4.96	4.01	16.16	$C_{13}H_{17}NO_8S_2$	41.15	4.52	3.69	16.90
XIIc	46.15	4.06	11.51	11.89	$C_{10}H_{12}N_2O_4S$	46.87	4.72	10.93	12.51
XIIIc	41.52	4.44	10.14	10.76	$C_{10}H_{12}N_2O_6S$	41.66	4.20	9.72	11.12

Table 3. (Contd.)

Comp. no.	Solvent	Chemical shifts δ, ppm
VIIIa	Acetone-d_6	3.56–3.75 m (5H), 4.07–4.20 m (1H), 5.17 d (1H) (11.0), 7.31–7.48 m (5H), 8.90 d (1H) (2.0), 9.02 d (1H) (2.0)
VIIIb	Acetone-d_6	3.75–3.85 m (8H), 4.00–4.15 m (1H), 5.16 d (1H) (11.1), 6.95 d (2H) (8.6), 7.38 d (2H) (8.6), 8.89 d (1H) (2.2), 9.03 d (1H) (2.2)
VIIIc	Acetone-d_6	2.94 s (6H), 3.60–3.72 m (5H), 3.90–4.05 m (1H), 5.02 d (1H) (11.0), 6.72 d (2H) (8.5), 7.28 d (2H) (8.5), 8.89 d (1H) (2.0), 9.03 d (1H) (2.0)
VIIId	Acetone-d_6	3.62–3.78 m (5H), 4.10–4.25 m (1H), 5.29 d (1H) (11.3), 7.44 d (2H) (8.9), 7.52 d (2H) (8.9), 8.91 d (1H) (2.1), 9.05 d (1H) (2.1)
VIIIe	Acetone-d_6	3.61–3.75 m (5H), 4.10–4.25 m (1H), 5.18 d (1H) (10.3), 7.19–7.21 m (2H), 7.45–7.58 m (2H), 8.90 d (1H) (2.0), 9.04 d (1H) (2.0)
VIIIf	Acetone-d_6	3.64 s (3H), 3.70–3.81 m (2H), 4.26–4.45 m (1H), 5.44 d (1H) (11.0), 7.80 d (2H) (8.8), 8.29 d (2H) (8.8), 8.92 d (1H) (2.2), 9.05 d (1H) (2.2)
VIIIg	Acetone-d_6	3.63 s (3H), 3.70–3.80 m (2H), 4.12–4.30 m (1H), 5.36 d (1H) (11.0), 7.41 m (1H), 7.93 m (1H), 8.55 m (1H), 8.67 m (1H), 8.91 d (1H) (2.1), 9.04 d (1H) (2.1)
IXa	Acetone-d_6	1.16 (t, 3H) (7.1), 1.58 s (3H), 3.74–3.83 m (5H), 4.08–4.22 m (2H), 4.41–4.49 m (1H), 6.95 d (2H) (8.8), 7.32 d (2H) (8.8), 8.90 d (1H) (2.3), 9.05 d (1H) (2.3)
IXb	Acetone-d_6	1.15 t (3H) (7.2), 1.60 s (3H), 3.77–3.87 m (2H), 4.10–4.22 m (2H), 4.47–4.57 m (1H), 7.12–7.22 m (2H), 7.40–7.53 m (2H), 8.90 d (1H) (2.3), 9.06 d (1H) (2.3)
IXc	Acetone-d_6	1.15 t (3H) (7.2), 1.70 s (3H), 3.87–3.93 m (2H), 4.12–4.19 m (2H), 4.57–4.62 m (1H), 7.39–7.45 m (1H), 7.89–7.94 m (1H), 8.55– 8.62 m (2H), 8.91 d (1H) (2.3), 9.08 d (1H) (2.3)
XVIa	Acetone-d_6	3.33–3.39 m (1H), 3.58 s (3H), 3.84–3.92 m (2H), 5.01 d (1H) (8.5), 7.14 t (2H) (8.1), 7.34 t (2H) (7.9), 7.67 d (2H) (8.5), 7.92 d (2H) (8.5), 8.87 d (1H) (1.9), 9.24 d (1H) (1.9)
XVIb	Acetone-d_6	0.93 s (3H), 1.02 s (3H), 2.27 non (1H) (8.0), 3.35 d (2H) (1.9), 3.65 s (3H), 3.72–3.79 m (1H), 4.10–4.18 m (2H), 5.08 d (1H) (8.5), 7.19 t (2H) (8.1), 7.53 t (2H) (7.9), 8.90 d (1H) (1.9), 9.01 d (1H) (1.9)
XVIc	Acetone-d_6	1.25 d.d (6H) (1.9, 8.1), 3.52–3.57 m (1H), 3.60 s (3H), 3.67–3.73 m (1H), 3.78 s (3H), 3.98–4.02 m (1H), 4.10–4.14 m (1H), 4.98 d (1H) (8.5), 6.94 d (2H) (8.5), 7.35 d (2H) (8.5), 8.88 d (1H) (1.9), 8.96 d (1H) (1.9)
XIVa	$CDCl_3$	2.58 s (3H), 3.76 s (3H), 3.80 s (2H), 7.53 d (2H) (8.5), 7.82 d (2H) (8.5), 8.39 d (1H) (1.9), 8.90 d (1H) (1.9)
XIVb	$CDCl_3$	1.09 s (3H), 1.14 s (3H), 2.34 non (1H) (8.0), 2.81 s (3H), 3.09 d (2H) (8.0), 3.78 s (3H), 3.85 s (2H), 8.49 d (1H) (1.9), 8.75 d (1H) (1.9)
XIVc	$CDCl_3$	1.27 s (3H), 1.35 s (3H), 2.78 s (3H), 3.32 sept (1H) (8.0), 3.78 s (3H), 3.83 s (2H), 8.38 d (1H) (1.9), 8.69 d (1H) (1.9)
XVa	$CDCl_3$	2.89 s (3H), 3.68 s (3H), 4.22 s (2H), 7.58 d (2H) (8.1), 7.84 d (2H) (8.1), 9.11 d (1H) (1.9), 9.33 d (1H) (1.9)
XVb	$CDCl_3$	1.11 s (3H), 1.16 s (3H), 2.39 non (1H) (8.0), 3.11 d (2H) (1.9), 3.15 s (3H), 3.72 s (3H), 4.31 s (2H), 9.14 d (1H) (1.9), 9.20 d (1H) (1.9)
XVc	$CDCl_3$	1.31 s (3H), 1.38 s (3H), 3.18 s (3H), 3.41 sept (1H) (8.0), 3.71 s (3H), 4.31 s (2H), 9.15 d (2H) (1.5)
XIIc	$CDCl_3$	1.43 d (6H) (10), 2.56 s (3H), 3.62 sept (1H) (9.9), 8.29 d (1H) (1.9), 8.38 d (1H) (1.9)
XIIIc	$CDCl_3$	1.39 d (6H) (10), 2.90 s (3H), 3.38 sept (1H) (9.9), 8.78 d (1H) (1.9), 9.10 d (1H) (1.9)

and its orthogonal arrangement with respect to the 5,7-dinitrophenyl ring plane. Protons of the latter fragment appear at δ 8.91 and 9.05 ppm. As follows from the above data, the methoxycarbonyl group on C^2 is equatorial (δ_{OMe} 3.66 ppm). Taking into account that the ^{1}H NMR parameters of the dihydrothiopyran fragment in **VIIId** and in the other thiochroman 1,1-dioxides are similar, we assume diaxial *trans*-orientation of 2-H and 3-H in **VIII** and **XVI** and, by analogy, of 2-Me and 3-H in **IX**.

EXPERIMENTAL

The melting points were determined on a Boetius device at a heating rate of 4 deg/min. The IR spectra were recorded on a Specord M-80 spectrometer from samples pelleted with KBr. The mass spectra (electron impact, 70 eV) were run on a Kratos MS-30 instrument. The ^{1}H NMR spectra were obtained on a Bruker AC-200 spectrometer. The ^{1}H NMR spectra of **VIIId** were recorded at 30°C on a Bruker DRX-500 spectrometer (500.13 MHz); acetone-d_6 was used as solvent, and TMS, as internal reference. NOESY experiment was performed according to the Bruker standard technique. The chemical shifts were measured with an accuracy of ±0.01 ppm, and ^{1}H–^{1}H coupling constants, with an accuracy of ±0.1 Hz. The progress of reactions was monitored by HPLC with a Liquochrom Model 2010 chromatograph (eluent MeCN–H_2O, 3 : 1; Silasorb 18 reversed phase).

2-(Alkoxycarbonyl-R-methylsulfonyl)-4,6-dinitrotoluenes **V** and **VI** (R = H, Me) were synthesized from 2,4,6-trinitrotoluene according to the procedure reported in [5]; 2-R′-sulfonyl-4,6-dinitrotoluenes **XIIIa** and **XIIIb** were synthesized as described in [5, 6]. Previously unknown sulfide **XIIc** and its oxidation product, sulfone **XIIIc**, were prepared from TNT following the corresponding standard procedures from [5]: the reaction of TNT with 2-propanethiol was carried out for 24 h at 20°C; yield of sulfide **XIIc** 50%, mp 32–33°C (from hexane); the oxidation of **XIIc** with a mixture of 35% hydrogen peroxide and acetic acid on heating (0.5 h) gave sulfone **XIIIc**, yield 87%, mp 108–109°C; the ^{1}H NMR spectra and analytical data of compounds **XIIc** and **XIIIc** are given in Table 3.

2-(Methoxycarbonylmethylthio)-4-R′-sulfonyl-6-nitrotoluenes XIVa–XIVc (*general procedure***).** A mixture of 0.02 mol of 2-R′-sulfonyl-4,6-dinitrotoluene **XIIIa**, **XIIIb**, or **XIIIc**, 1.88 ml (0.02 mol) of methyl 2-mercaptoacetate (**I**), 2.76 g (0.02 mol) of potassium carbonate, and 20 ml of *N*-methylpyrrolidine was stirred for 24 h at room temperature (~20°C). The mixture was poured into cold water and acidified with dilute hydrochloric acid, and the precipitate was filtered off, dried in air, and recrystallized from appropriate solvent (Tables 2, 3).

2-(Methoxycarbonylmethylsulfonyl)-4-R′-sulfonyl-6-nitrotoluenes XVa–XVc (*general procedure***).** A mixture of 0.02 mol of 2-(methoxycarbonylmethylthio)-4-R′-sulfonyl-6-nitrotoluene **XIVa**, **XIVb**, or **XIVc**, 6.85 ml of 35% aqueous hydrogen peroxide, and 40 ml of glacial acetic acid was heated for 1 h under reflux. The mixture was cooled, and the precipitate was filtered off and dried in air or in a drying box under reduced pressure. The products, except for **XVc**, required no additional purification (Tables 2, 3).

3-Aryl-2-methoxycarbonyl-5,7-dinitrothiochroman 1,1-dioxides VIIIa–VIIIg, 3-aryl-2-ethoxycarbonyl-2-methyl-5,7-dinitrothiochroman 1,1-dioxides IXa–IXc, and 3-aryl-2-methoxycarbonyl-7-nitro-5-R′-sulfonylthiochroman 1,1-dioxides XVIa–XVIc (*general procedure***).** Piperidine, 0.1 ml, and glacial acetic acid, 0.11 ml, were added to a mixture of 0.01 mol of 2-(alkoxycarbonyl-R-methylsulfonyl)-4-X-6-nitrotoluene **V**, **VI**, or **XVa–XVc** (R = H, Me; X = NO_2, R′SO_2) and 0.011 mol of aromatic aldehyde **VII** in 100 ml of benzene. The mixture was heated for 2–5 h under reflux in a flask equipped with a Dean–Stark trap. The progress of the reaction was monitored by HPLC. When the initial sulfone disappeared, the mixture was cooled to ~7–8°C, and the precipitate was filtered off, washed with a dilute aqueous solution of sodium chloride and water, dried in air, and recrystallized from appropriate solvent (Tables 2, 3).

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