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NITRATION OF SOME 2-SUBSTITUTED THIONAPHTHENES

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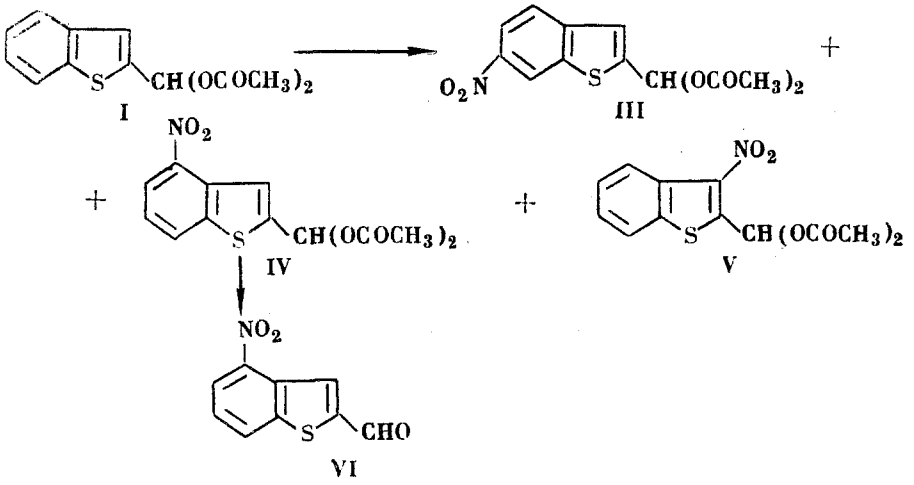
A study is made of the nitration of thionaphthene-2-aldehyde, its diacetate, and of 2-(ω-nitrovinyl)thionaphthene. UV and IR spectroscopy show that nitration of thionaphthene-2-aldehyde in acetic anhydride gives a mixture of 3-nitrothionaphthen-2-aldehyde diacetate, 4-nitrothionaphthene-2-aldehyde diacetate, and 6-nitrothionaphthene-2-aldehyde diacetate in the ratios 10:66:24, while nitration of thionaphthene-2-aldehyde diacetate gives a mixture of 3-nitrothionaphthene-2-aldehyde diacetate, 4-nitrothionaphthene-2-aldehyde diacetate, and 6-nitrothionaphthene-2-aldehyde diacetate in the ratios 36:38:26. Nitration of 2-(ω-nitrovinyl)thionaphthene gives 4-nitro-2-(ω-nitrovinyl)thionaphthene.

Nitro compounds with reactive substituents ortho to the nitro group, are often used for preparing heterocyclic systems. In the course of work on the synthesis of condensed heterocyclic systems based on thiophene, thionaphthene-2-aldehyde diacetate (I) and 2-(ω-nitrovinyl)thionaphthene (II) were nitrated. 3-Nitro derivatives would be expected to be the main products in both cases, as the groups $-CH(OAc)_2$ and $-CH{=}CH-NO_2$ have I orientating effects [1, 2] and 2-methylthionaphthene is known [3] to nitrate at position 3.



However, nitration of I gave a mixture of isomeric mononitro compounds III and IV, with different melting points, but whose analyses corresponded to the mononitro compound I. The IR spectra of both compounds contain valence vibration bands of the NO_2 group, and also of ester C–O and C=O groups.

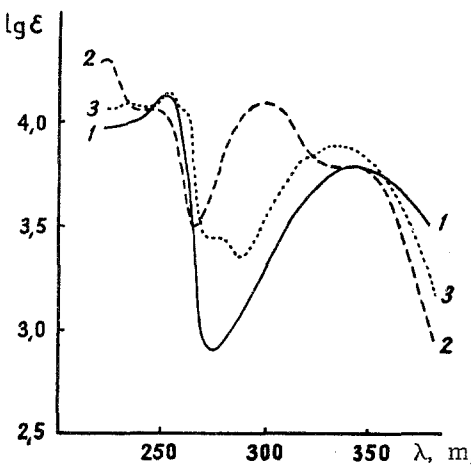


Fig. 1. UV spectra: 1) 4-nitrothionaphthene [5]; 2) III; 3) IV.

Compounds III and IV had different melting points and different IR spectra to the previously synthesized 3- and 5-nitrothionaphthene-2-aldehyde diacetates [4]. As the present authors previously showed that introduction of the methylene diacetate group into a nitrothionaphthene does not alter the character of its UV spectrum, to determine the position of the nitro group in III and IV, their UV spectra were compared with that of 4-nitrothionaphthene [5] (Fig. 1), when it was found that III is not 4-nitrothionaphthene-2-aldehyde diacetate. Consequently, III is the 6- or 7-nitro derivative of I. The choice between these structures was made from IR spectroscopic data.

The IR spectra of condensed aromatic systems in the region of in-plane C–H vibrations can be considered as comprising bands characteristic of each aromatic ring with a particular type of substituent [6]. Thus, in the present case the absence of intense bands in the 750-810 cm^{-1} region of the IR spectrum of III (Fig. 2), indicates the absence of three consecutive hydrogen atoms in the benzene ring [8] of thionaphthene. At the same time, the intense band at 862 cm^{-1} can be ascribed to out-of-plane deformation vibrations of two adjacent hydrogen atoms [8], and the intense band at 903 cm^{-1} to vibrations of an isolated hydrogen atom [8]. The medium intensity band at 842 cm^{-1} can, according to avail-

able data [7], be ascribed to vibrations of an isolated hydrogen atom of the thiophene ring (the spectrum of I has an intense band at 846 cm^{-1}). Hence it can be concluded that III is 6-nitrothionaphthene-2-aldehyde diacetate.

The IR spectrum of IV has two intense absorption bands at 810 and 820 cm^{-1} (see Fig. 2), while the spectrum of the corresponding nitroaldehyde VI has an intense band at 815 cm^{-1}. These bands can be ascribed to the vibrations of three consecutive hydrogen atoms in the benzene ring. The known 3, 4-dinitrothionaphthene [9] which also has three consecutive hydrogen atoms, has only a single high-intensity band at 812 cm^{-1} in its IR spectrum. Such high frequencies can be explained by the ring's containing a group which is strongly electron-accepting, NO_2[8].

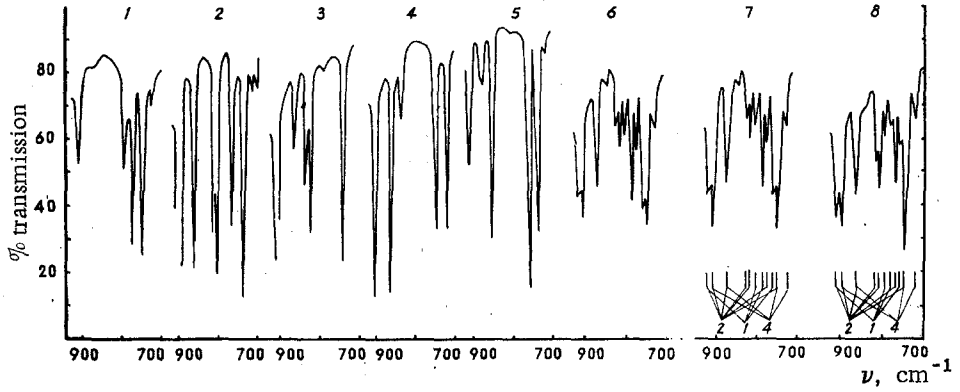


Fig. 2. IR spectra: 1) V; 2) IV; 3) 5-nitrothionaphthene-2-aldehyde diacetate; 4) III; 5) I; 6) artificial mixture of III, IV, and V; 7) mixture of isomers obtained by nitrating I; 8) mixtures of isomers obtained by nitrating thionaphthene-2-aldehyde.

However, the presence of three consecutive hydrogen atoms in the benzene ring does not make it possible to decide whether IV is a 4- or a 7-nitro derivative. But considering how close together the UV absorption curves of IV and 4-nitrothionaphthene are (see Fig. 1), this isomer can be considered to be 4-nitrothionaphthene-2-aldehyde diacetate. This is even more likely, since the π electron density and the free valence number, as calculated by the MO–LCAO method, are lower at position 7 than at position 5 [5]. Moreover the absence of the 5 isomer in the nitration products (taking into account the orientating effect of the $CH(OAc)_2$ group) is a reason for thinking formation of the 7 nitro isomer at least improbable.

Comparison of the IR spectrum of the reaction product with the spectra of the individual nitroaldehyde diacetates (Fig. 2) showed that the mixture contained not only III and IV, but also the 3-nitro isomer V. To ascertain the ratios of these isomeric nitro compounds the mixed nitration products from I, and also from thionaphthene-2-aldehyde were analyzed quantitatively, using the method of [10]. Analyses were made from the IR absorption spectra of substances compressed with potassium bromide (4 mg substance in 800 mg KBr), and the accuracy was ±4%. The bands selected for analytical purposes for the 6-, 3-, and 4-nitro isomers were, respectively, at 723, 780, and 810 cm^{-1}. The following ratios (as %) were found for the isomeric nitrothionaphthene-2-aldehyde diacetates in the mixtures isolated:

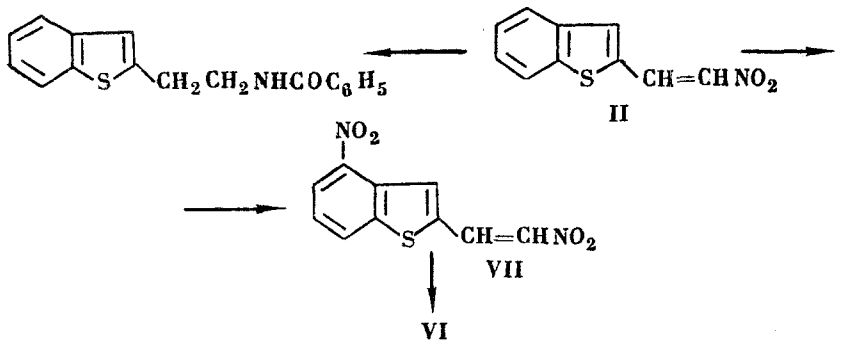
	III	IV	V
By nitrating thionaphthene-2-aldehyde	24	66	10
By nitrating thionaphthene-2-aldehyde diacetate 1	26	38	36

The results obtained were checked with an artificial mixture of III, IV, and V in the ratios 2.5 : 4.0 : 3.5, and the IR spectrum of this mixture and that obtained by nitrating I, were identical (see Fig. 2). Prolonged nitration of I led to isolation of a dinitro derivative of thionaphthene-2-aldehyde diacetate, whose structure was not determined.

Another compound subjected to nitration, II, is prepared by condensing thionaphthene-2-aldehyde with nitromethane. The IR spectrum of II has NO_2 group bands, a strong band at 1620 cm^{-1}, characteristic of the C=C bond conjugated with an aromatic ring [8], as well as bands at 930-950 cm^{-1} (in-plane deformation vibrations of vinyl group hydrogen atoms) indicating that II exists in the trans form [8]. Lithium aluminum hydride reduction of II gave β-(2-thionaphthenyl)ethylamine, isolated as its benzoyl derivative; the latter has previously been prepared by another method [11].

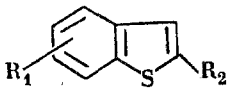
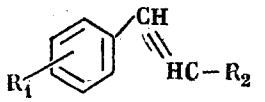
4-Nitro-2-(ω-nitrovinyl)thionaphthene (VII) was obtained when II was nitrated under conditions similar to those used for nitrating I. The IR spectrum of VII shows two strong absorption bands at 780 and 790 cm^{-1} (vibrations of three consecutive hydrogen atoms in the benzenoid ring), two bands at 960 and 980 cm^{-1} (vibrations of trans hydrogen atoms of the vinyl group), and also a band at 1625 cm^{-1} (C=C conjugated with the aromatic ring). The absence of strong bands in the 810-860 cm^{-1} region (vibrations of two adjacent hydrogen atoms in the benzene ring) makes it possible to conclude that the nitro group is at position 4 or position 7 in the thionaphthene ring. The structure of VII was determined by oxidizing it with potassium permanganate in acetone [12] to 4-nitrothionaphthene-2-aldehyde, identical with a speci-

men of VI prepared by hydrolysis of IV.



From study of the UV spectra of a number of heterocyclic cystems [13, 14] it can be assumed that the position of the K band of a number of substituted thionaphthenes is basically determined by the chromophoric system comprising an aromatic ring and the C=C bond conjugated to it. So the corresponding substituted styrenes (Table) can serve as model compounds for thionaphthene derivatives. The K band position for VIII and IX has been calculated from a rule derived in a paper [18]. The data given show that the K bands of III and p-nitrostyrene match well. The non-matching of the K bands for VII and IX (position of NO_2 group in VII the same as in IV) once again indicates the correctness of the structure with the nitro group at position 4 in the thionaphthene ring, while the isomer with the nitro group in position 7 should have the same K band value as it has in IX.

Position of the K Band for a Number of Thionaphthene Derivatives and for the Corresponding Styrenes

	λ_{max}, mμ (lg ε)		λ_{max}, mμ (lg ε)
R_1=H, R_2=CHO	294—296(4.1)	R_1=H, R_2=CHO[15]	289(4.4)
R_1=H, R_2=C_6H_5[16]	297(4.4)	R_1=H, R_2=C_6H_5[15]	295(4.4)
R_1=H, R_2=CH=CHNO$_2$ **(II)**	354(4.4)	R_1=H, R_2=CH=CHNO$_2$ **(VIII)**	~350(≥4.2)
R_1=6-NO$_2$, R_2=CH(OCOCH$_3$)$_2$ **(III)**	300(4.1)	R_1=*p*-NO$_2$, R_2=H[17]	301(4.2)
R_1=4-NO$_2$, R_2=CH=CHNO$_2$ **(VII)**	344—346(3.8)	— —	—
— —	—	R_1=*m*-NO$_2$, R_2=CH=CHNO$_2$ **(IX)**	~310(≥4.2)

Experimental

The UV spectra were determined with a SF-4 spectrophotometer; the solvent was ethanol.

The IR spectra of solid compounds, pressed into discs with potassium bromide (4 mg substance in 800 mg KBr), were recorded by an UR-10 spectrophotometer.

Thionaphthene-2-aldehyde diacetate (I). This was prepared in 74% yield by acetylating thionaphthene-2-aldehyde [19] by the method of [20]. Mp 92-93° (from alcohol). Found: C 59.1; 58.7; H 4.63, 4.64; S 12.0, 12.0%. Calculated for $C_{13}H_{12}O_4S$: C 59.1; H 4.54; S 12.1%. UV spectrum, λ_{max}, mμ (lg ε): 228 (4.43), 260 (4.00), 292 (3.45), 300, (3.44). IR spectrum, ν cm^{-1}: 1200, 1245 (ester C–O); 1760 (ester C=O).

2-(ω-Nitrovinyl)thionaphthene (II). A solution of 0.47 g (12 mmole) sodium hydroxide in 17 ml water was dropped into a mixture of 1.8 g (11 mmole) thionaphthene-2-aldehyde, 0.7 g (11 mmole) nitromethane and 8 ml methanol kept at about 0°, the whole then stirred for 30 min, and poured into 6 ml 6 N hydrochloric acid, the precipitate filtered off, and washed with water. Yield 2.2 g (77%), mp 158-159° (from alcohol). Found: C 58.6, 58.8; H 3.53, 3.51; N 6.91, 6.98%. Calculated for $C_{10}H_7NO_2S$: C 58.5; H 3.44; N 6.82%. UV spectrum, λ_{max}, mμ (lg ε): 224 (4.34), 260 (3.89), 354 (4.40). IR spectrum, ν cm^{-1}: 1330, 1520 (NO_2).

N-Benzoyl-β-(2-thionaphthenyl)ethylamine. 2 g (9.8 mmole) II was added in portions to 40 ml of an ethereal solution of lithium aluminum hydride [prepared from 1 g (126 mmole) lithium hydride and 8 g (30 mmole) aluminum bromide] at such a rate as to keep the ether gently refluxing, after which the products were refluxed for 2 hr, and then decomposed, first with water, then with alkali. The ether solution was evaporated, the residue treated with 2 N hydrochloric acid, and extracted with ether. Then the ether was distilled off, and the residue benzoylated. The benzoyl derivative of the amine was isolated, and washed with water. Yield 1.6 g (60%), mp 153-154°. The literature [11] gives mp 153-154.5°.

Nitration of thionaphthene-2-aldehyde (I) diacetate. 0.65 ml nitric acid (d 1.5) was dropped into stirred suspension of 1.3 g (5 mmole) I in 8 ml glacial acetic acid plus 1 ml acetic anhydride maintained at −5° to 0°. After an hour the mixture was poured onto ice, and the oily product triturated with 1.5 ml methanol plus 0.5 ml acetone, after which it was pressed out on a filter. Yield 0.75 g (50%) mp 77-85°. For quantitative analysis of this mixture, see above. After crystallization from alcohol, the crystals were dissolved in alcohol plus acetone, heat being used. Diamond-shaped crystals came down on cooling. When crystallization was complete, the mother liquor (A) was decanted rapidly, and the crystalline part transferred to a filter, where it was washed with alcohol. For analysis the 4-nitrothionaphthene-2-aldehyde diacetate was further twice recrystallized from alcohol. Yield 0.2 g (13%), mp 149.5-150.5°. Found: N 4.78, 4.82%. Calculated for $C_{13}H_{11}NO_6S$: N 4.56%. UV spectrum, λ_{max} mμ (lg ε): 253 (4.15), 278 (3.46), 336 (3.90). IR spectrum ν cm^{-1}: 1350, 1520 (NO_2); 1220, 1250 (ester C–O); 1765 (ester C=O).

Further cooling of the mother liquor (A) gave flaky crystals of 6-nitrothionaphthene-2-aldehyde diacetate (III), which were filtered off and recrystallized from alcohol. Yield 0.08 g (5%), mp 120-121°. Found: N 4.70, 4.80%. Calculated for $C_{13}H_{11}NO_6$: N 4.56%. UV spectrum, λ_{max}, mμ (lg ε): 224 (4.30), 240-244 (4.06), 300 (4.09), 334-340 (3.79). IR spectrum, ν cm^{-1}: 1345, 1515 (NO_2); 1190, 1230 (ester C–O); 1770 (ester C=O).

Nitration of thionaphthene-2-aldehyde. 0.26 ml nitric acid (d 1.5) was added dropwise to a solution of 0.3 g (1.9 mmole) aldehyde in 2 ml acetic anhydride plus 2 ml acetic acid at 0°. After 20 min the products were allowed to stand at room temperature for 2 hr, then poured onto ice, the oily product dissolved in 0.5 ml acetone, and 1 ml methanol added. The precipitate was filtered off, washed on the filter with methanol, yield 0.17 g (30%), mp 130-133°. For quantitative analysis of the mixture, see above. Recrystallization from alcohol gave 0.07 g (12%) 4-nitrothionaphthene-2-aldehyde diacetate (IV), mp 149-150°.

4-Nitro-2-(ω-nitrovinyl)thionaphthene (VII). A mixture of 2 ml nitric acid (d 1.5) and 3 ml acetic anhydride was dropped into a suspension of 1 g (4.9 mmole) II in 5 ml acetic anhydride at −5°, the II gradually dissolving, and an orange precipitate being formed. After continuing the stirring for a further 1 hr, the precipitate was filtered off, washed with 5 ml cold methanol, and 5 ml ether, and dried in a vacuum over phosphorus pentoxide and alkali. Yield 0.60 g (50%), mp 141-143° (from ethyl acetate). Found: C 48.1, 48.4; H 2.45, 2.41; N 11.3, 11.4%. Calculated for $C_{10}H_6N_2O_4S$: C 48.0; H 2.42; N 11.2%. UV spectrum λ_{max}, mμ (lg ε): 252-254 (4.06), 344-346 (3.81). IR spectrum, ν cm^{-1}: 1340, 1530 (NO_2).

4-Nitrothionaphthene-2-aldehyde (VI). 2 ml 10% sulfuric acid was added to a hot solution of 0.24 g (0.8 mmole) IV in 8 ml alcohol, and the whole refluxed for 30 min. The yellow, needle-shaped crystals which separated on cooling were separated off, and washed with water, yield 0.14 g (87%), mp 209-210° (from acetic acid). Found: C 52.4, 52.6; H 2.47, 2.50; N 6.55, 6.70; S 15.6, 15.4%. Calculated for $C_9H_5NO_3S$: C 52.2; H 2.43; N 6.76; S 15.5%. UV spectrum λ_{max}, mμ (lg ε): 232 (4.11), 262 (4.09), 278 (3.92), 336-338 (3.95). IR spectrum, ν cm^{-1}: 1350, 1525 (NO_2); 1675 (C=O); 2845 (C–H in aldehydes). Semicarbazone, mp 308-310° (from acetic acid). Found: N 21.1, 21.3%. Calculated for $C_{10}H_8N_4O_3S$: N 21.2%.

B. A saturated acetone solution of potassium permanganate was added to a solution of 0.57 g (2.3 mmole) VII in 25 ml acetone cooled in ice, until a permanent red color appeared. After filtering the solution was concentrated in a vacuum, the residue washed with water and a small amount of methanol. Yield 0.11 g (24%), mp 208-209° (from acetic acid). Mixed mp with VI prepared as above undepressed.

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