

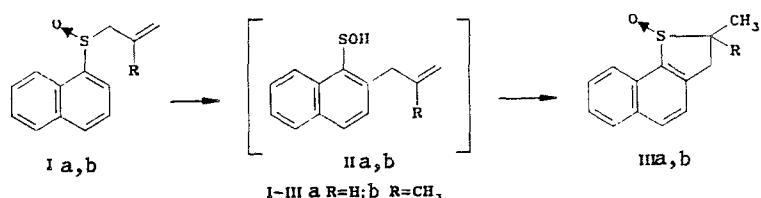
2,3-DIHYDRONAPHTHO[1,2-b]THIOPHENE 1-OXIDES IN THE SYNTHESIS OF
2,3-DIHYDRONAPHTHO- AND NAPHTHO[1,2-b]THIOPHENES

N. V. Fedorov, A. V. Anisimov,
and E. A. Viktorova

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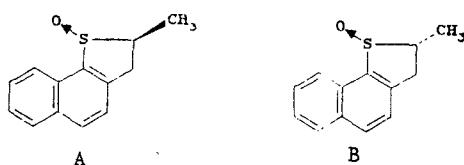
2,3-Dihydronaphtho[1,2-b]thiophene 1-oxides, obtained by thermolysis of alkyl 1-naphthyl sulfoxides, are reduced by lithium aluminum hydride to 2,3-dihydronaphtho[1,2-b]thiophenes, whereas under the influence of acetic and trifluoroacetic anhydrides they form naphtho[1,2-b]thiophenes.

Compounds of the dihydronaphtho- and naphthothiophene series are of interest as subjects that model individual components of the higher fractions of high-sulfur petroleum oils [1] and potential starting substances for the synthesis of compounds that have the properties of pesticides, light sensitizers, etc. In the present research to obtain 2,3-dihydronaphtho- and naphtho[1,2-b]thiophenes we used transformations of 2,3-dihydronaphtho[1,2-b]thiophene 1-oxides IIIa, b, which are formed as a result of 3,3-sigmatropic rearrangement of the corresponding allyl 1-naphthyl sulfoxides Ia, b, through the intermediate sulfenic acids IIa, b with their subsequent cyclization [2, 3]:



The cyclization of sulfenic acids IIa, b leads to the formation of only five-membered heterocycles, while such high selectivity could not be achieved in the 3,3-sigmatropic rearrangement of allyl 1-naphthyl sulfides: mixtures of dihydro-naphthothiophenes and dihydro-naphthothiopyrans were always obtained as a result of the cyclization of the intermediately formed thiols [2, 3].

The existence of two pairs of diastereomers A and B, which differ with respect to the mutual orientation of the methyl group and the oxygen atom of the sulfinyl group, is possible for sulfoxide IIIa, which has two asymmetric centers:



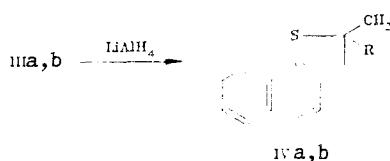
It is known [4] that in the PMR spectra the signal of the protons of the methyl group of the trans isomer of 2-methyl-2,3-dihydronaphtho[1,2-b]thiophene 1-oxide is shifted slightly to a strong-field region as compared with the signal of the protons of the methyl group of the cis isomer; this makes it possible to make quantitative evaluation of the ratio of the cis and trans isomers. Two incompletely separated doublets, which correspond to the methyl groups of the diastereomeric pairs A and B of sulfoxide IIIa, are found in the PMR spectrum of our synthesized 2-methyl-2,3-dihydronaphtho[1,2-b]thiophene 1-oxide (IIIa) (360 MHz) at 1.53-1.56 ppm. The equal intensities of these signals make it possible to assume that diastereomers of sulfoxide IIIa are formed in a ratio of 1:1.

M. V. Lomonosov Moscow State University, Moscow 119899. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1629-1633, December, 1989. Original article submitted July 25, 1988.

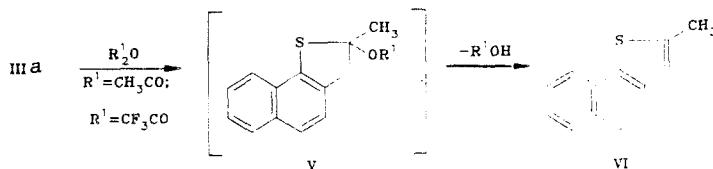
TABLE 1. Results of Transformations of 2,3-Dihydronaphtho-[1,2-b]thiophene 1-Oxides IIIa, b

Sulf-oxide	Solvent	Reagent	Exptl. time	Temp., °C	Yields of reaction products, %		
					VI	VIII	IV a, b
IIIa	Ac ₂ O	Ac ₂ O	3	130	93	—	—
	CH ₂ Cl ₂	(CF ₃ CO) ₂ O	4	40	75	—	—
	Diethyl ether	LiAlH ₄	2	31	—	—	96
IIIb	Ac ₂ O	Ac ₂ O	7	130	—	—	80
	CH ₂ Cl ₂	(CF ₃ CO) ₂ O	4	40	—	63	—
	Diethyl ether	LiAlH ₄	2	34	—	—	98

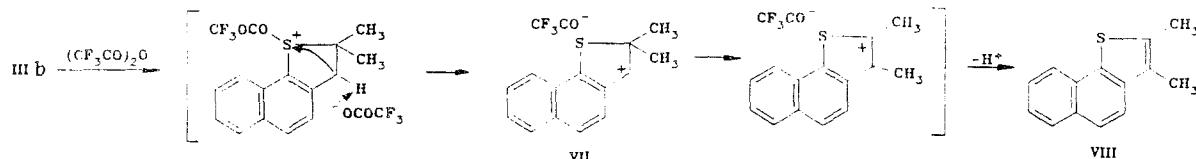
The reduction of thiophene 1-oxides IIIa, b with lithium aluminum hydride leads to the formation of the corresponding 2,3-dihydronaphtho[1,2-b]thiophenes IVa, b in high yields (Table 1):



It is known that the Pummerer reaction of saturated sulfoxides is a convenient method for obtaining vinyl sulfides [5-7]. To obtain naphtho[1,2-b]thiophenes, thiophene 1-oxides IIIa, b were subjected to the Pummerer reaction; acetic and trifluoroacetic anhydrides were used as the reagents. Under the influence of both acetic and trifluoroacetic anhydride IIIa gives 2-methylnaphtho[1,2-b]thiophene (VI) in good yields (up to 90%) (Table 1):



2,3-Dimethylnaphtho[1,2-b]thiophene (VIII) is formed in high yield in the reaction of IIIb (R = CH₃) with trifluoroacetic anhydride. One of the steps in this process is evidently 1,2 migration of the methyl group in intermediate cation VII:



Only one compound — 2,2-dimethyl-2,3-dihydronaphtho[1,2-b]thiophene (IVb) — was obtained as a result of the transformation of sulfoxide IIIb in excess acetic anhydride. The formation of this sulfide is confirmed by the complete coincidence of its spectrum with the PMR spectrum of dihydronaphthothiophene IVb, obtained in the reduction of sulfoxide IIIb with lithium aluminum hydride.

The principal pathway of the mass-spectral fragmentation of IVa, b, VI, and VIII is the characteristic (for methyldihydronaphtho- and methylnaphthothiophenes) successive elimination of one or two methyl groups with the formation of [M - CH₃]⁺ and [M - 2CH₃]⁺ ions and the elimination of an [SH][·] radical. For all of the examined compounds except IVb the molecular-ion peak has the maximum intensity; this is in good agreement with the literature data [2, 3, 8]. For methyldihydronaphthothiophenes IVa, b one observes virtually equal intensities of the peaks of M⁺ and [M - CH₃]⁺ ions, while for methylnaphthothiophenes VIII and VI the intensities of the peaks of the [M - CH₃]⁺ ions are 68% and 6% of the intensities of the corresponding peaks of the molecular ions. This constitutes evidence that the formation of the [M - CH₃]⁺ ion occurs considerably more readily for saturated heterocyclic structures IVa, b than for the unsaturated analogs VI and VIII. The same principle is also observed for the formation of [M - 2CH₃]⁺ ion in the spectra of IVb and VIII.

TABLE 2. Properties of the Compounds Obtained

Compound	PMR spectrum, δ , ppm	Mass spectrum, m/z (intensity, %)	IR spec- trum, ν , cm^{-1}	Yield, %
Allyl 1-naphyl sulfoxide (Ia)	3.20...3.91 (2H, m, SCH_2); 4.85...6.00 (3H, m, $\text{CH}=\text{CH}_2$); 7.30...8.10 (7H, m, arom)	216 (M^+ , 14), 200 (2), 175 (100), 147 (34), 127 (26), 115 (31), 103 (7), 77 (13), 63 (7), 51 (8), 41 (13)	1030 (S=O)	97
2-Methylallyl 1-naphthyl sulf oxide (Ib)	1.73 (3H, s, CH_3); 3.10...3.68 (2H, q, SCH_2); 4.70...4.78 (2H, d, $=\text{CH}_2$); 7.20...8.10 (7H, m, arom)	230 (M^+ , 22), 213 (1), 199 (1), 175 (100), 167 (6), 147 (20), 127 (32), 115 (20), 101 (4), 77 (8), 55 (56)	1030 (S=O)	94
2-Methyl-2,3-dihydronephtho[1,2-b]thiophene oxide (IIIa)	1.41...1.51 (3H, m, CH_3); 2.81...3.58 (2H, m, CH_2); 3.59...4.44 (1H, q, CH); 7.27...7.90 (5H, m, arom)	216 (M^+ , 100), 199 (87), 184 (80), 165 (28), 152 (23), 138 (18), 128 (16), 115 (46), 92 (21), 79 (19), 63 (14), 40 (39)	1040 (S=O)	45
2,2-Dimethyl-2,3-dihydronephtho[1,2-b]thiophene oxide (IIIb)	1.21...1.46 (6H, d, 2CH_3); 2.71...3.65 (2H, q, CH_2); 7.21...8.50 (7H, m, arom.)	230 (M^+ , 26), 213 (68), 198 (32), 187 (30), 165 (14), 139 (8), 117 (100), 83 (84), 47 (66), 35 (34)	1030 (S=O)	46
2-Methyl-2,3-dihydronephtho[1,2-b]thiophene (IVa)	1.37 (3H, d, CH_3); $J=6.0$ Hz; 2.75...3.70 (2H, m, CH_2); 4.00...7.00 (1H, m, CH); 7.00...7.85 (6H, m, arom)	200 (M^+ , 100), 199 (40), 185 (94), 171 (14), 165 (38), 152 (40), 141 (32), 139 (34), 127 (12), 115 (24), 109 (36), 92 (60), 79 (20), 63 (22), 51 (12), 39 (18)	—	96
2,2-Dimethyl-2,3-dihydronephtho[1,2-b]thiophene (IVb)	1.55 (6H, s, 2CH_3); 3.29 (2H, s, CH_2); 7.10...7.90 (6H, m, arom)	214 (M^+ , 99), 199 (100), 184 (42), 165 (15), 152 (8), 139 (7), 128 (4), 107 (12), 92 (15), 76 (6), 63 (4), 40 (8)	—	98
2-Methylnaphtho[1,2-b]thiophene (VI)	2.40 (3H, s, CH_3); 6.71 (CH, s, β -H thiophene ring); 7.10...8.00 (6H, m, arom)	198 (M^+ , 100), 197 (78), 183 (8), 172 (15), 165 (19), 143 (10), 128 (6), 117 (12), 99 (26), 88 (14), 64 (14), 59 (18), 41 (85)	—	93
2,3-Dimethyl-naphtho[1,2-b]thiophene (VIII)	1.65 (6H, d, 2CH_3); $J=8.5$ Hz; 7.0...7.91 (6H, m, arom)	212 (M^+ , 100), 197 (68), 183 (6), 178 (9), 165 (9), 152 (6), 117 (3), 98 (21), 87 (12), 73 (19), 59 (21), 44 (50), 39 (38)	—	63

It has been previously noted that a characteristic feature of the mass spectra of methyl-dihydrothiophenes is the formation of an $[\text{M} - 1]^+$ ion due to the elimination of a hydrogen atom [9]. In the case of naphthothiophene IVb the intensity of the peak of the $[\text{M} - \text{H}]^+$ ion is 38% of the intensity of the molecular ion, while it does not exceed 2% for 2,2-dimethyl-2,3-dihydronephtho[1,2-b]thiophene (IVa). In our opinion, this constitutes evidence that the formation of the $[\text{M} - 1]^+$ ion occurs through the elimination of a methylidyne hydrogen atom, while the contribution of the methylene protons of the heterocyclic system to the formation of the $[\text{M} - 1]^+$ ion is minimal.

EXPERIMENTAL

The IR spectra of films of the compounds with the use of KBr glasses were recorded with KHS-22 and UR-20 spectrometers. The PMR spectra (20-25% solutions in CCl_4) were recorded with a Tesla spectrometer with an operating frequency of 60 MHz with tetramethylsilane (TMS) as the internal standard. The accuracy in the determination of the chemical shifts was ± 0.01 ppm, while the accuracy in the determination of the spin-spin coupling constants (SSCC) was ± 0.5 Hz. The chromatographic mass-spectrometric analysis was carried out with a Finnigan MAT-112S spectrometer at an ionizing energy of 80 eV with a glass capillary column ($l = 25$ m, $d = 0.25$ mm) with OV-101 as the stationary phase under isothermal conditions at 210°C and under temperature-programming conditions from 80°C to 250°C (heating rate $5^\circ\text{C}/\text{min}$) with helium as the carrier gas.

The isolation and purification of the starting substances and the reaction products were carried out by column and thin-layer chromatography with a loose layer of sorbent (sil-pearl UV-254). Hexane or hexane- CCl_4 -ether (47:43:10) was used as the eluent for the isolation and purification of the sulfides; for the sulfoxides we used chloroform-hexane-acetone (5:1:1) or the method of gradient elution in a hexane-chloroform system.

The results of elementary analysis of the synthesized compounds for C, H, and S were in agreement with the calculated values.

Sulfoxides Ia, b. These compounds were obtained by oxidation of the corresponding sulfides with 28% hydrogen peroxide in glacial acetic acid [10, 11].

Sulfoxides IIIa, b. A solution of 0.01 mole of sulfoxide Ia, b in a 10-fold to 15-fold excess of DMF (by volume) was heated in an argon atmosphere at 130°C. At the end of the experiment the reaction mixture was dissolved in chloroform, and the solution was washed successively with water, 10% HCl solution, and 10% sodium bicarbonate solution. The organic layer was dried with Na_2SO_4 , and the chloroform was removed by distillation to give the corresponding dihydronaphthothiophene 1-oxide IIIa, b.

2,3-Dihydronaphtho[1,2-b]thiophenes IVa, b. The reduction of sulfoxides IIIa, b to sulfides IVa, b was carried out by a general method [12]. Sulfoxide III (the molar ratio of lithium aluminum hydride to the sulfoxide was 1.5:1) was added to a solution of lithium aluminum hydride in absolute ether, and the mixture was refluxed for 2 h, after which it was cooled, and the unchanged lithium aluminum hydride was neutralized with a small amount of water. The ether layer was dried with Na_2SO_4 , the ether was removed by distillation, the residue was analyzed. The isolation of sulfides IVa, b was carried out by TLC on plates with a loose layer of sorbent. The properties of the compounds obtained are presented in Table 2.

Naphtho[1,2-b]thiophenes VI and VIII. A) The starting sulfoxide was dissolved in a large excess of purified acetic anhydride, and the system was purged with argon for 15 min and then heated to the experimental temperature. At the end of the reaction the acetic anhydride was removed by vacuum distillation, the residue was dissolved in chloroform, and the solution was washed successively with 10% HCl (two 10-15 ml portions), water (two 20-ml portions), and 10% sodium bicarbonate solution (one 20-ml portion). The chloroform extract was dried with Na_2SO_4 , the chloroform was removed by distillation, and the residue was separated on plates with a loose layer of sorbent.

B) A solution of trifluoroacetic anhydride in methylene chloride was added with stirring to a solution of the starting sulfoxide in excess methylene chloride (the molar ratio of the sulfoxide to trifluoroacetic anhydride was 1:15), after which the reaction mixture was heated to the boiling point. At the end of the experiment the reaction mixture was worked up as described in method A. The properties of the compounds obtained are presented in Table 2.

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