was solved by direct methods and was refined by anisotropic full matrix least squares for all nonhydrogen atoms. All hydrogen atoms, found in difference maps, were refined isotropically. Refinement in the final stages used 1909 reflections with $I \geq 5\sigma$. The final R factors were $R = 0.035$ and $R_w = 0.049$. All calculations were done on an IBM PDP-11/23PLUS using SDP-PLUS programs [7]. The coordinates of nonhydrogen and hydrogen atoms are given in Table 3.

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NITRILE OXIDES OF THE THIOPHENE SERIES: INFLUENCE OF STERIC FACTORS ON STABILITY AND REACTIVITY IN REACTIONS OF 1,3-DIPOLAR CYCLOADDITION

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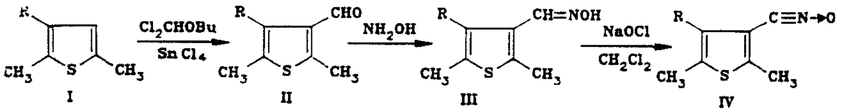
The synthesis of a series of di- and trialkyl-substituted thiophenecarbonitrile oxides is described. Their addition to styrene is studied together with the quantitative evaluation of the influence of different alkyl groups on the rate of the 1,3-dipolar cycloaddition reaction by the method of competing reactions.

The first examples of nitrile oxides of the the thiophene series, the stability of which was determined by the presence of an electron-accepting substituent together with the C≡N→O group, were previously studied in our laboratory [1]. Moreover, there are well known examples of the aromatic series where the stability is determined by the steric effects of the two alkyl groups in the ortho positions relative to the nitrile oxide function. Thiophene analogs of such compounds are described below; the extent of the shielding influence of different alkyl groups on the stability of the substances and the rates of their reaction with styrene were evaluated quantitatively. The synthesis of the products was performed by the following scheme:



I—IV a R=H; b $R=CH_3$; c $R=CH_2CH_3$; d $R=CH(CH_3)_2$

We also undertook attempts to synthesize analogs of the compounds (IV) in which both the alkyl groups adjoining the nitrile oxide group differ from methyl. It was to be expected that the most sterically hindered compound would have two tertbutyl groups. Taking into account the known ease of cleavage of the tert-butyl groups during electrophilic substitution in the presence of Lewis acids, it is impossible to synthesize such a compound by the formylation of 2-methyl-3,5-di-tertbutylthiophene (V) under the conditions utilized for the isolation of the aldehydes (II). Therefore, it was planned to carry out the bromination of compound (V)

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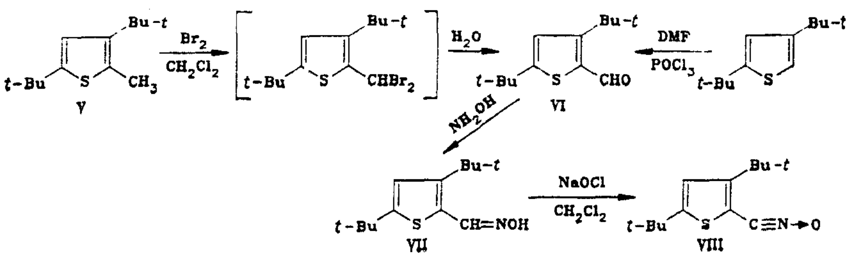
TABLE 1. ^{1}H NMR Spectra of the Aldehydes (II), the Oximes (III), and the Nitrile Oxides (IV) of the Thiophene Series

Compound	Solvent	Chemical shifts, ppm				SSCCs, Hz
		2-CH_3	5-CH_3	3-R	4-R	
IIc	CCl_4	2,58	2,20	9,86	1,00 t ; 2,70 q	7,5
IId	CCl_4	2,53	2,25	10,03	1,22 d; 3,38 m	7,5
IIIa	$(CD_3)_2CO$	2,32	2,25	8,03; 9,98	6,82	—
IIIb	$CDCl_3$	2,43	2,23	8,15; 9,05	2,12	—
IIIc	$CDCl_3$	2,35	2,15	8,13; 9,01	0,97 t; 2,53 q	7,5
IIId	$CDCl_3$	2,32	2,12	8,09; 9,46	1,14 d ; 3,10 m	7,0
IVb	$CDCl_3$	2,38	2,20	—	2,02	—
IVc	CCl_4	2,48	2,28	—	1,14 t; 2,53 q	7,5
IVd	CCl_4	2,46	2,28	—	1,28 d; 3,04 m	7,5

TABLE 2. ^{13}C NMR Spectra of the Compounds (IVb-d) in $CDCl_3$

Compound	Chemical shifts, ppm							
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	2-CH_3	5-CH_3	4-R	CNO
IVb	143,71	110,76	133,14	130,71	14,22	12,71	12,53	32,02
IVc	143,94	109,71	139,50	130,35	14,13	14,03	20,71 (CH_2); 12,31 (CH_3)	33,60
IVd	144,91	108,15	143,23	129,69	14,25	13,01	28,05 (CH); 21,69 (CH_3)	34,20

with the subsequent exchange of halogen by lithium, and the treatment of the organolithium compound with dimethylformamide. However, this objective was not successfully attained: the halogen atom enters the 2-CH_3 group. The hydrolysis of the reaction mixture led to the isolation of 3,5-di-tertbutylthiophene-2-aldehyde (VI), which is identical to the product of the formylation of 2,4-di-tertbutylthiophene in the conditions of the Vilsmeier reaction. By analogy to the method described above, the aldehyde (VI) was converted, via the oxime (VII), to the nitrile oxide (VIII), the properties of which were compared with those of the nitrile oxides (IVa-d).



The IR spectra of the nitrile oxides (IVa-d) and (VIII) contain absorption bands of the $C{\equiv}N{\rightarrow}O$ group at 2300 and 1370 cm^{-1} as well as the absorption bands of the thiophene ring in the region of 1560...1575 cm^{-1}. In the UV spectra of the compounds (IVb-d), there are absorption maxima at 226 and 263 nm (ε 11,000...12,000). The nitrile oxide (VIII) has the λ_{max} 210 nm (ε 9200) and 286 nm (ε 11,100). The data of ^{1}H NMR and mass spectrometry conform with the proposed structures of (IVb-d) and (VIII) (Table 1). The close values of the chemical shifts of the carbon atoms of the nitrile oxide groups in the ^{13}C NMR spectra of the compounds (IVb-d) evidently indicate the very insignificant electronic influence of different alkyl substituents at the position 4 on the indicated groups (Table 2). This permits the limitation of only considering the steric effects in the discussion of the stability and reactivity of the nitrile oxides (IV).

The substances obtained possess varying stability* which is evidently determined by the degree of shielding of the nitrile oxide function by the alkyl groups. Thus, compound (IVa), which only has one methyl substituent adjoining the $C{\equiv}N{\rightarrow}O$ group, is only stable in the course of several hours, and the product (VIII), which is shielded by the tertbutyl group,

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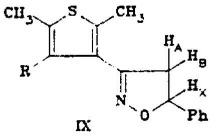
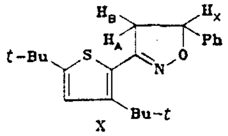
*The stability signifies the capacity of the compound to retain the physicochemical properties at 25°C [2].

is stable for not more than 10 days. The nitrile oxide (IVb), in which the nitrile oxide function is disposed between two methyl groups, is stable for 3 weeks. The substitution of the methyl group by ethyl at the position 4 of the thiophene ring increases the stability of (IVc) insignificanty. The most stable of the compounds obtained is 2,5-dimethyl-4-isopropylthiophene-3-nitrile oxide (IVd), which is kept for more than 2 months without observable changes.

The synthesized compounds (IVa-d) and (VIII) readily enter into the 1,3-dipolar cycloaddition (1,3-DCA) reaction with styrene to form high yields of the thienyl-substituted isoxazolines (IXa-d) and (X).



IX



X

A single regioisomer was formed in each case; its structure was unambiguously shown using ^1H NMR spectroscopy. The shift of the signals of the H_X protons by almost 2 ppm to weaker field by comparison with the signals of the H_A and H_B protons of the cycloadducts indicates the formation of the regioisomers (IXa-d) and (X) (Table 3). Analogous ^1H NMR spectra are given by cycloadducts of mesitonitrile oxide [2] and the previously described nitrile oxides of the thiophene series [1] with styrene.

A series of kinetic measurements by the method of competing reactions was performed with the object of quantitatively evaluating the influence of steric factors on the reactivity of nitrile oxides of the thiophene series in the 1,3-DCA reactions with styrene (Table 4). Mesitonitrile oxide was utilized as a reference substance; its rate constant equals $2.92 \cdot 10^{-4}$ liter·mole^{-1}·sec^{-1} for the reaction with styrene in CCl_4 at 20°C [2].

The compounds (IV) and (VIII) proved to be more active than mesitonitrile oxide. This is evidently a consequence of the differing geometry of the rings, with the higher outer bond angles in thiophene by comparison with benzene; this leads, in the first case, to the lower shielding of the reaction center and correspondingly to an increase in the reactivity. An increase in the volume of the alkyl substituent at the position 4 of the thiophene ring lowers the rate of the cycloaddition: in the transition (IVb) → (IVd), the k_{rel} decreases threefold. The influence of steric factors is also clearly shown by the comparison of the compounds (IVa) and (VIII): the rate of the 1,3-DCA reaction for the nitrile oxide (VIII), which is shielded by the tertbutyl group, is lower than that for the compound (IVa). At the same time, it should be noted that both these substances, which have only one substituent adjoining the $C{\equiv}N{\rightarrow}O$ group, react more rapidly with styrene than the remaining nitrile oxides which are shielded by two alkyl groups. Therefore, the change in the extent of shielding appreciably influences both the stability and the reactivity of the nitrile oxides of the thiophene series.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer using KBr tablets and the solutions in CCl_4. The UV spectra were recorded on a Specord UV-vis spectrometer. The ^1H NMR spectra were taken on the Tesla BS-467 (60 MHz) and Bruker WM-250 (250 MHz) spectrometers. The ^{13}C NMR spectra were taken on a Bruker WM-250 (62.89 MHz) spectrometer for the solutions in $CDCl_3$. The mass spectra were taken on a Varian MAT CH-6 instrument with the direct input of the sample at the ion source, the ionizing voltage of 70 eV, and the emission current of 100 μA. The chromatographic analyses were carried out on the LKhM-80 chromatograph with a flame-ionization detector, stainless steel columns 2 mm by 2 m, and 5% SE-30 on Chromaton N-AW-DMCS, at the temperature of 160°C with the gas carrier of nitrogen at the rate of 20 ml/min.

The Initial 2,3,5-Trimethyl- and 2,5-Dimethyl-3-ethylthiophenes (Ib, c). These were obtained by the Kishner reduction of 2,5-dimethylthiopene-3-aldehyde and 2,5-dimethyl-3-acetothienone [3, 4].

2,5-Dimethyl-3-isopropylthiophene (Id). This was obtained from 2,5-dimethylthiophene and isopropyl chloride in the presence of the equivalent amount of aluminum chloride; the solvent was CH_2Cl_2 (by analogy with the method of [5]). The stable σ-complex – 2,5-dimethyl-3-

isopropyl-2H-thiophenium tetrachloraluminate — is formed directly in the course of the reaction. The ^{1}H NMR spectrum (CH_2Cl_2) is as follows: 1.40 ppm [dd, 6H, $(CH_3)_2CH$, $J_{H\text{-}2Me}$ = 3 Hz], 1.90 ppm (d, 3H, 2-Me, $J_{2H\text{-}2Me}$ = 7.5 Hz), 3.18 ppm (d, 3H, 5-Me, $J_{2H\text{-}5Me}$ = 3 Hz), 3.66 ppm (m, 1H, Me_2CH), and 7.48 ppm (s, 1H, 4-H). The signal of 2-H is superimposed with the solvent signal. The treatment of the σ-complex with water gives the compound (Id) with the yield of 75%. The ^{1}H NMR spectrum of (Id) (CCl_4) is as follows: 2.15 ppm [d, 6H, $(\underline{CH_3})_2CH$, J = 7 Hz], 2.22 ppm (s, 3H, 2-Me), 2.31 ppm (s, 3H, 5-Me), 2.84 ppm (m, 1H, Me_2CH, $\underline{J}$ = 7 Hz), and 6.33 ppm (s, 1H, 4-H). The properties of compound (Id) are in accord with those described in [5].

2,4-Di-tertbutylthiophene (cf. [6]). Into the suspension of 8.2 g (61 mmole) of $AlCl_3$ in the solution of CH_2Cl_2 at −78°C is passed a stream of dry HCl until saturation is effected; 12 g (61 mmole) of the mixture of 2,5- and 2,4-di-tertbutylthiophenes, obtained according to the method of [7], are then added dropwise. The reaction mixture is thawed out and left for 2 days at 20°C. The mixture is poured into water, and the organic layer is separated. It is washed with a 1% solution of KOH and water and dried. The solvent is distilled, and the residue is distilled in vacuo. The yield of 8.58 g (72%) of 2,4-di-tertbutylthiophene is obtained; it has the bp 89°C (10 mm Hg) and the n_D^{20} 1.4924, which corresponds to the data of [7]. The ^{1}H NMR spectrum (CCl_4) is as follows: 1.17 ppm [s, 9H, $(CH_3)_3C$], 1.27 ppm [s, 9H, $(CH_3)_3C$], 6.52 pppm (d, 1H, 5-H), and 6.59 ppm (d, 1H, 3-H, J_{35} = 1.5 Hz).

3,5-Di-tertbutyl-2-methylthiophene (V). To the solution of 38.2 g (0.39 mole) of 2-methylthiophene and 86 ml (72.2 g, 0.78 mole) of tertbutyl chloride in 350 ml of CH_2Cl_2 are added, dropwise with stirring for 1 h, 90 ml (198 g, 0.78 mole) of $SnCl_4$ so that the temperature of the reaction mixture should not exceed 0°C. The mixture is then stirred at room temperature for 5 h; it is poured into 500 ml of 10% HCl. The organic layer is separated and washed with water and 5% aqueous KOH. The solvent is distilled off, and the residue is steam distilled. The distillate is extracted with ether, and the extract is dried with $MgSO_4$. The ether is distilled off; the distillation of the residue leads to the isolation of 63.6 g (77%) of compound (V) with the bp 80...85°C (4 mm of Hg stem) and the n_D^{20} 1.5020. Found: C 73.5, H 10.4, and S 15.1%. $C_{13}H_{22}S$. Calculated: C 74.2, H 10.4, and S 15.1%. The ^{1}H NMR spectrum (CCl_4) is as follows: 1.25 ppm [s, 18H, $(CH_3)_3C$], 2.33 ppm (s, 3H, CH_3), and 6.40 ppm (s, 1H, 3-H).

2,5-Dimethyl-4-alkylthiophene-3-aldehydes (IIb-d). To the solution of 0.1 mole of the 2,5-dimethyl-3-alkylthiophene (Ib-d) and 0.27 mole of $SnCl_4$ in 100 ml of methylene chloride is added, dropwise with stirring, 0.25 mole of α,α-dichloromethyl butyl ether so that the temperature of the reaction mixture should not exceed 5°C. At the completion of the addition of the ether, the cooling is removed, and the temperature of the reaction mixture is brought to room temperature for 40 min. The mixture is then boiled on a water bath with a reflux condenser with the periodic withdrawal of samples for GLC. After 3 h of boiling, the content of the initial trialkylthiophene (Ib-d) comprises less than 1% according to the GLC data. The reaction mass is poured onto a mixture of 500 cm^3 of ice and 50 ml of concentrated HCl. It is shaken in a separatory funnel until the disappearance of the violet color of the organic layer is evident; the organic layer is then separated. The aqueous layer is extracted with CH_2Cl_2, and the combined organic layers are carefully washed with a solution of Na_2CO_3 and water. After the distillation of the solvent, the product is steam distilled, and 5 liters of the distillate are collected. It is extracted with ether; the ether solution is dried with $MgSO_4$. The ether is distilled off, and the residue is distilled in vacuo. The characteristics of the aldehydes (IIb-d) are shown in the Tables 1 and 5.

3,5-Di-tertbutylthiophene-2-aldehyde (VI). A. To 10 ml of DMF are added 5 ml (55 mmole) of $POCl_3$ while cooling the mixture in ice. The mixture is heated for 15 min on a water bath at 80°C prior to cooling it again and adding 8.58 g (44 mmole) of 2,4-di-tertbutylthiophene dropwise. The mixture is heated on a water bath at 100°C for 5 h and is then poured into a solution of sodium acetate. The aqueous solution is extracted with chloroform, and the organic layer is washed with water until a neutral reaction is obtained. The solvent is distilled off, and the residue is distilled in vacuo. The yield of 7.24 g (74%) of a viscous light yellow liquid is obtained. The ^{1}H NMR spectrum (CCl_4) is as follows: 1.33 and 1.43 ppm [s, 9H, 3- and 5-$C(CH_3)_3$], 6.73 ppm (s, 1H, 4-H), and 10.13 ppm (s, 1H, CHO). The remaining characteristics can be seen in Table 5.

B. To the solution of 28.8 g (0.13 mole) of 3,5-di-tertbutyl-2-methylthiophene (V) in 600 ml of CH_2Cl_2 are added, dropwise with stirring and cooling in ice, 14 ml (41.6 g, 0.26 mole) of bromine such that the temperature of the solution should not rise above 0°C. The

TABLE 3. PMR Spectra of the Cycloadducts (IXa-d) and (X) in $CDCl_3$ (250 MHz)

Compound	Chemical shifts, ppm				SSCC, Hz			
	protons of the thiophene residue	H_A, q	H_B, q	H_X, q	C_6H_5, m	J_{AB}	J_{AX}	J_{BX}
IXa	2,41 (s, 3H, 2-CH_3); 2,65 (s, 3H, 5-CH_3); 6,68 (s, 1H, 4-H)	3,27	3,71	5,62	7,30...7,45	15,9	9,1	8,5
IXb	1,17 (s, 3H, 4-CH_3); 2,32 (s, 3H, 5-CH_3); 2,47 (s, 3H, 2-CH_3)	3,25	3,75	5,72	7,30...7,50	16,3	10,0	6,9
IXc	0,92 (t, 3H, 4-CH_3CH_2, J=7 Hz); 2,43 (q, 2H, 4-CH_3CH_2, J=7 Hz); 2,15 (s, 3H, 5-CH_3); 2,20 (s, 3H, 2-CH_3)	2,91	3,53	4,42	6,95...7,42	16,0	10,5	8,0
IXd	1,28 [d, 6H, 4-$(CH_3)_2CH$, J=7 Hz]; 2,33 (s, 3H, 5-CH_3); 2,42 (s, 3H, 2-CH_3); 3,02 [m, 1H, $(CH_3)_2CH$, J=7 Hz]	3,17	3,64	5,77	7,30...7,50	18,0	11,0	8,5
X	1,41 [m, 9H, 3-$(CH_3)_3C$]; 1,47 [s, 9H, 5-$(CH_3)_3C$]; 6,88 (s, 1H, 4-H)	3,33	3,77	5,71	7,30...7,50	15,0	11,3	8,8

TABLE 4. Relative Rates of the Reactions of Nitrile Oxides of the Thiophene Series (IVa-d) and (VIII) with Styrene in CCl_4 at 20°C

No. of experiment	1,3-Dipoles		A, mmole	B, mmole	Styrene, mmole	$k_{rel} = k_A/k_B$
	A	B				
1	IVb	MesCNO*	0,5	0,5	0,5	3,5
2	IVb	MesCNO	0,25	0,75	0,25	3,7
3	IVc	MesCNO	0,5	0,5	0,5	3,0
4	IVc	MesCNO	0,25	0,75	0,25	3,3
5	IVd	MesCNO	0,5	0,5	0,5	1,3
6	IVd	MesCNO	0,25	0,75	0,25	1,0
7	VIII	MesCNO	0,5	0,5	0,5	4,8
8	VIII	IVd	0,25	0,75	0,25	4,1 (4,7)**
9	IVa	IVd	5,0	5,0	5,0	6,1 (8,2)**

*MesCNO indicates mesitonitrile oxide.

**The values presented in the brackets were obtained by comparison with mesitonitrile oxide: $k_{rel} = k_A/k_{MesCNO}$.

reaction mixture is stirred for 5 h at 20°C, and is left during the night. The mixture is then poured into 500 ml of a 2% solution of $Na_2S_2O_3$. The organic layer is separated and washed with a 10% solution of NaOH and water, and is dried with $MgSO_4$. The solvent is distilled off, and the residue is distilled in vacuo prior to the isolation of 14.22 g (38%) of 3,5-di-tert-butylthiophene-2-aldehyde (VI).

2,5-Dimethyl-4-alkylthiophene-3-aldoximes (IIIa-d). The solution of 70 mmole of the aldehyde (IIa-d) in 50 ml of ethanol is stirred with the solution of 10.5 g (140 mmole) of hydroxylamine hydrochloride and 19 g (140 mmole) of sodium acetate in 50 ml of water; the mixture is heated to boiling and alcohol is added up to homogenization. The reaction mixture is boiled for 4 h prior to the double dilution with water. The precipitated residue is filtered off, washed with water, dried, and dissolved in the 1:3 mixture of ether-hexane prior to the filtration through a glass filter with silica gel (160/100 mesh, diameter 5 cm, depth of layer 5 cm). The filtrate is evaporated, and the residue is recrystallized. The characteristics of the oximes can be seen in the Tables 1 and 5.

3,5-Di-tertbutylthiophene-2-aldoxime (IIIe). This is obtained analogously. The ^1H NMR spectrum (CCl_4) is as follows: 1.47 ppm [s, 18H, 3- and 5-$C(CH_3)_3$], 6.70 ppm (s, 1H, 4-H), 8.60 ppm (s, 1H, –CH=), and 9.6 ppm (s, 1H, OH). The remaining characteristics can be seen in Table 5.

2,5-Dimethyl-4-alkylthiophene-3-nitrile Oxides (IVa-d). To the solution of 10 mmole of the aldoxime (IIIa-d) in 15 ml of CH_2Cl_2 are added, dropwise with intense stirring, 10 ml of a 12% solution of sodium hypochlorite (1.2 g, 16 mmole) so that the temperature of the mixture

TABLE 5. Characteristics of the Aldehydes (II) and (VI), the Aldoximes (III) and (VII), the *Nitrile Oxides* (IV) and (VIII), and the Isoxazolines (IX) and (X)

Compound*[1]	bp, °C (mm of Hg stem) or mp, °C*[2]	M⁺	IR spectrum, cm⁻¹	Found, %				Empirical formula	Calculated, %				Yield, %
				C	H	N	S		C	H	N	S	
IIc*[3]	97 (5)	—	1680, 1560	64,5	7,3	—	18,7	$C_9H_{12}OS$	64,3	7,2	—	19,1	55
IId*[4]	106 (5)	—	1685, 1560	66,2	8,1	—	17,2	$C_{10}H_{14}OS$	65,9	7,7	—	17,6	72
VI*[5]	120 (5)	—	1650, 1520	69,6	9,5	—	14,0	$C_{13}H_{20}OS$	69,6	8,5	—	14,3	74
IIIb	103...104	169	3300, 1635	57,1	6,9	8,0	18,5	$C_8H_{11}ONS$	56,8	6,6	8,3	18,9	88
IIIc	85...90	183	3300, 1625	58,7	7,1	7,5	17,2	$C_9H_{13}ONS$	59,0	7,1	7,6	17,5	86
IIId	72...73	197	3300, 1665	60,3	8,0	7,0	15,9	$C_{10}H_{15}ONS$	60,9	7,7	7,1	16,3	80
VII	127...128	239	3300, 1625	66,0	9,3	6,1	13,4	$C_{13}H_{21}ONS$	65,2	8,8	5,9	13,4	83
IVa	28...30 (decomp.)	—	2300, 1590, 1400	—	—	—	—	—	—	—	—	—	70
IVb*[6]	72...73	167	2300, 1575, 1370	57,9	5,6	8,2	18,9	C_8H_9ONS	57,5	5,4	8,4	19,2	93
IVc*[6]	59,5...61	181	2300, 1570, 1370	59,6	5,9	7,8	17,5	$C_9H_{11}ONS$	59,6	6,1	7,7	17,7	72
IVd	36...37	195	2300, 1560, 1370	61,8	6,8	7,0	16,2	$C_{10}H_{13}ONS$	61,5	6,7	7,2	16,4	75
VIII	67...71	237	2300, 1630, 1370	66,6	9,1	5,9	12,9	$C_{13}H_{19}ONS$	65,8	8,1	5,9	13,5	87
IXa	175...180 (0,5)*[7]	257	1590, 1300, 1240, 830	69,8	5,8	5,3	12,2	$C_{15}H_{15}ONS$	70,0	5,9	5,4	12,5	73
IXb	180 (0,5)*[7]	271	1585, 1305, 1240, 850	71,0	6,3	5,4	11,7	$C_{16}H_{17}ONS$	70,8	6,3	5,6	11,8	85
IXc	180...185 (0,5)*[7]	285	1550, 1300, 1255, 850	72,0	6,5	5,2	11,1	$C_{17}H_{19}ONS$	71,5	6,7	4,9	11,2	81
IXd	67...68	299	1605, 1305, 830	71,9	7,0	4,7	10,5	$C_{18}H_{21}ONS$	72,2	7,1	4,7	10,7	92
X	86	341	1535, 1305, 1245, 890, 850	73,9	7,9	4,0	8,7	$C_{21}H_{27}ONS$	73,9	8,0	4,1	9,4	82

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*[1] The characteristics of the compounds (IIa,b) and (IIIa) are in accord with those described in the works [3, 4, 10]; the yields of (IIa), (IIb), and (IIIa) are 78%, 57%, and 70%, respectively.

*[2] The compounds (IIIc,d) and (VII) are recrystallized from hexane; (IVb) is recrystallized from the 1:1 mixture of pentane-hexane; (IVc), (VIII), (IXd), and (X) are recrystallized from methanol.

*[3] n_D^{20} 1.5515.

*[4] n_D^{20} 1.5410.

*[5] n_D^{20} 1.5358

*[6] They can be purified by sublimation at 60°C (5 mm of Hg); the yield is 60%.

*[7] The bath temperature is indicated.

should not exceed 0°C. After the addition of the oxidant, the reaction mixture is stirred for 20 min more. The organic layer is separated, and the aqueous layer is extracted with CH_2Cl_2. The combined organic layers are washed with water and dried with Na_2SO_4; the solvent is distilled off. The residue is recrystallized. The characteristics of the nitrile oxides (IVa-d) are presented in Tables 1 and 5.

3,5-Di-tertbutylthiophene-2-nitrile Oxide (VIII). This is obtained by the method described. The ^1H NMR spectrum ($CDCl_3$) is as follows: 1.38 ppm [s, 9H, $C(CH_3)_3$], 1.40 ppm [s, 9H, $C(CH_3)_3$], and 6.73 ppm (s, 1H, 4-H). The remaining characteristics can be seen in Table 5.

5-Phenyl-3-(2,5-dimethyl-4-alkyl-3-thienyl)-2-isoxazolines (IXa-d) and 5-Phenyl-3-(3,5-di-tertbutyl-2-thienyl)-2-isoxazoline (X). One of the compounds (IVb-d) or (VIII) (3 mmole) and 3.2 mmole of styrene are dissolved in 10 ml of CCl_4, and the mixture is left at 20°C. After 2 days, the solution is evaporated, and the residue in 3 ml of hexane is applied to a column with silica gel 100/160 mesh (diameter 14 mm, height of layer 30 cm). The solution is performed with hexane, collecting 80 ml of the solution, and then with ether, collecting 100 ml of the solution. The ether fraction is evaporated; the residue is distilled in vacuo or recrystallized. The cycloadduct (IXa) of the unstable nitrile oxide (IVa) is obtained in situ by the method of [8]; the method of purification is analogous to that indicated above. The yields and characteristics of the compounds (IXa-e) and (X) can be seen in the Tables 3 and 5.

Determination of the Reactivity of the Nitrile Oxides by the Method of Competing Reactions. A. The case for the stable nitrile oxides (IVb-d) and (VIII). The solution of 0.25... 0.5 mmole of styrene, 0.25...0.5 mmole of the nitrile oxide (IVb-d) or (VIII), and 0.75...0.5 mmole of mesitonitrile oxide is dissolved in 1.2 ml of CCl_4 and left at 20°C. After 2 days, 0.2 ml of the solution is removed prior to the addition of 0.2 ml of $CDCl_3$ (the standard for ^1H NMR) and the taking of the ^1H NMR spectrum.

B. The case for the unstable nitrile oxide (IVa). To the ice-cooled solution of 0.776 g (5 mmole) of the aldoxime (IIIa), 0.986 g (5 mmole) of the aldoxime (IIId), and 0.521 g (5 mmole) of styrene in 24 ml of CCl_4 are added, dropwise with energetic stirring, 10 ml of a 12% solution of NaOCl (1.1 g, 17 mmole) at a temperature of <7°C. The mixture is stirred at this temperature for 30 min; the temperature is then raised to room temperature for 30 min. After this, the stirring is discontinued. After 2 days, the organic layer is separated, washed with water, and dried with $MgSO_4$; the ^1H NMR spectrum of the solution obtained is taken.

The calculation of the k_{rel} was carried out according to [9]. The ratios of the final and initial concentrations of the nitrile oxides were determined from the integral curves of the ^1H NMR spectra. The signals of the protons of the 4-R group of the thiophene ring were utilized for the calculation along with the ABX-protons fo the cycloadducts and the aromatic protons of the mesityl residue.

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