1-Methyl-2-[3-(1-methyl-4-tert-butyl-6-phenyl-1,4-dihydropyridinylid-2-ene)-prop-1-en-1-yl]-4-tert-butyl-6-phenylpyridinium perchlorate (XV) was obtained in a similar way as IX, using pyrylocyanin XI.

1-Methyl-2-[5-(1-methyl-4-tert-butyl-6-phenyl-1,4-dihydropyridinylid-2-ene)-1,3-pentadien-1-yl]-4-tert-butyl-6-phenylpyridinium perchlorate (XVI) was obtained a similar way as IX from pyrylocyanin XII.

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EFFECT OF ELECTRONIC FACTORS ON THE DIMERIZATION AND ISOMERIZATION OF SUBSTITUTED NITRILE OXIDES OF THE THIOPHENE SERIES

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Sterically hindered, stable 3-thiophenecarbonitrile oxides containing electron-accepting groups (SO_2R, Br) in the 2- or 4-position are converted to substituted 4,5-dithienylfuroxanes when boiled in benzene or toluene, whereas trialkyl-substituted 3-thiophenecarbonitrile oxides isomerize quantitatively to the corresponding isocyanates.

It is known that heating nitrile oxides above the limit of their thermal stability leads to two concurrent reactions: dimerization to furoxanes and isomerization to isocyanates [1]. Here the isomerization to the isocyanate characteristically predominates for sterically hindered, aromatic nitrile oxides [1].

In the present work we have studied the effect of the nature of the substituent on the direction of these conversions in sterically hindered, stable 3-thiophenecarbonitrile oxides Ib-j containing electron-donor or electron-acceptor substituents in the 2, 4, and 5 positions [2, 3] and also in nitrile oxide II [3].

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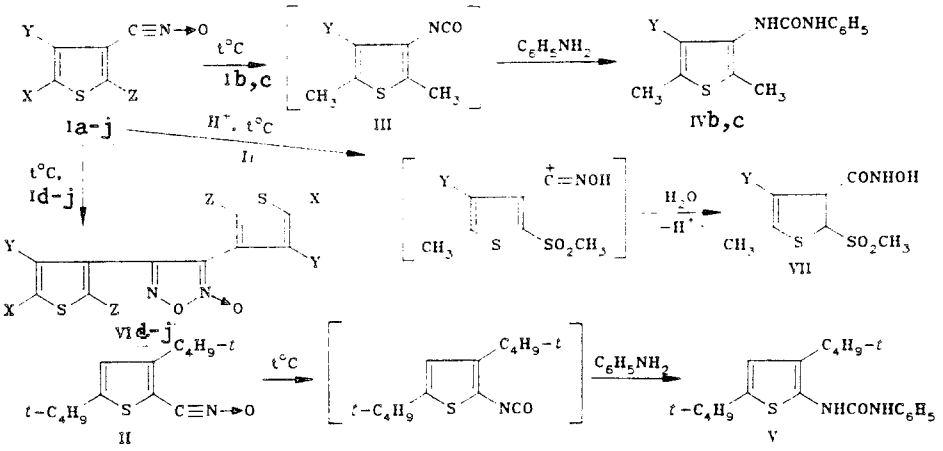
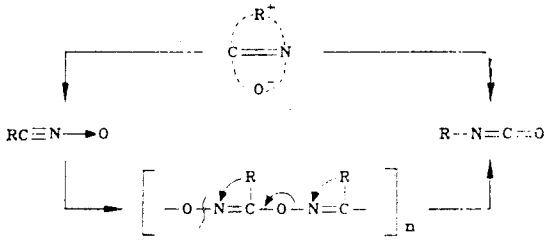


I, IV, VI a X=Z=CH_3, Y=H, b X=Y=Z=CH_3, c X=Z=CH_3, Y=*i*-CH_3H_7, d X=CH_3, Y=H, Z=SO_2CH_3, e X=OCH_3, Y=H, Z=SO_2CH_3, f X=Y=H, Z=$SO_2C_4H_9$-*t*, g X=CH_3, Y=Br, Z=SO_2CH_3, h X=Y=H, Z=$SO_2C_2H_5$, i X=Z=SO_2CH_3, Y=H, j X=CH_3, Y=Br, Z=SCH_3

It was found that trialkylsubstituted nitrile oxides Ib, c, which are stable at 20°C, are almost completely converted to isocyanates III on boiling in benzene. 3,5-Di-tert-butyl-2-thiophenecarbonitrile oxide (II), with strong screening of the nitrile oxide function, is converted to the isocyanate on boiling in toluene. The resultant isocyanates were characterized as mixed ureas IVb, c and V. Unstable 2,5-dimethyl-3-thiophenecarbonitrile oxide (Ia), which dimerizes to the furoxane even at 20°C, forms a mixture of 62% furoxane VIa and 11% isocyanate at 80°C.

Thus, in the case of alkyl-substituted nitrile oxides of the thiophene series, Ib, c and II are found to be analogous to the corresponding derivatives of the aromatic series, in particular to mesitonitrile oxide (MNO), which quantitatively rearranges to mesityl isocyanate at 100°C [4, p. 132].

In the presence of a catalytic amount of CF_3COOH, the process is sharply accelerated, the isomerization of nitrile oxide Ib in benzene at 20°C is over in 20 min as against 5 h for MNO [5]. This is in agreement with currently accepted ideas about the mechanism of this rearrangement as an intra- [6, 7] or intermolecular process [5] that takes place with the synchronous breaking and formation of bonds, and also with the migration of the aryl residue R to the electronegative nitrogen atom which is initiated by nucleophilic catalysis at C^+ or protonation at O^-.



It can be assumed that electron-donor substituents in the thiophene or benzene rings, increasing the nucleophilicity of the migrating radical, promote isomerization. The difference in the rates of rearrangement of nitrile oxide Ib and MNO, mentioned above, can obviously be explained by the greater ability of the thiophene ring to stabilize the transition state, due to the participation of the heteroatom in the delocalization of positive charge.

A different picture is seen when nitrile oxides Id-i, containing an electron-accepting alkylsulfonyl group in the 2 position are heated. In all of the cases we studied, furoxanes VId-i were obtained regardless of the nature of the substituent in the 5 or 4 position (X = H, OCH_3; Y = H, Br). In their IR spectra there were strong absorption bands in the 1600-1620 cm^{-1} region and intense [M – 30] and [M – 60] peaks in the mass spectra that are characteristic of the decomposition of molecular ions of aryl-substituted furoxanes with the loss of NO and N_2O_2 fragments. In not a single case was an admixture of isocyanates observed. From 4-bromo-substituted nitrile oxide Ij, furoxane VIj, containing 2% of isocyanate IVj, was obtained in an analogous manner.

The effect of the nature of the substituents shows up also in the reaction of nitrile oxide Id in the presence of CF_3COOH since, unlike trialkyl-substituted nitrile oxide Ib, hydrolysis of the reaction mixture does not give the isocyanate but rather 3-

TABLE 1. Characteristics of Substituted N-Thienyl-N'-phenylurea IVa–c, j and V

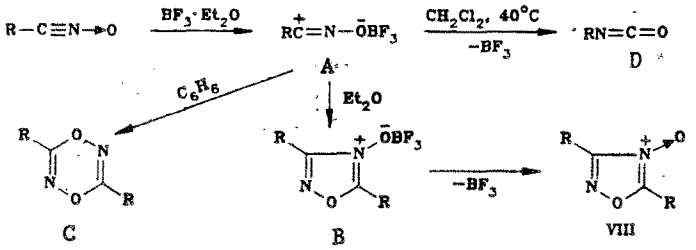
Compound	Empirical formula	mp, °C	IR spectra, ν cm^{-1} (KBr)	Mass spectra, m/z (I, %)	Yield, %
IVa	$C_{13}H_{14}N_2OS$	213...215	3300, 1640, 1600, 1560	246 (45, M^+), 203 (13), 127 (100), 93 (45)	11
IVb	$C_{14}H_{16}N_2OS$	232...234	3284, 1638, 1598, 1556	260 (100, M^+), 185 (10), 167 (30), 140 (100), 93 (65)	96
IVc	$C_{16}H_{20}N_2OS_2$	205...206	3300, 1650, 1600, 1560	288 (45, M^+), 153 (13), 152 (13), 127 (100), 93 (45)	91
IVj	$C_{13}H_{13}BrN_2OS_2$	231...233	3300, 1640, 1600, 1565	358/356 (41, M^+), 265/263 (13), 224/222 (100), 93 (47)	2
V	$C_{19}H_{26}N_2OS$	221...223	3300, 1650, 1598, 1555	330 (30, M^+), 315 (25), 337 (10), 222 (30), 211 (28), 196 (100), 93 (25)	85

TABLE 2. Characteristics of Furoxanes VIa, d–j

Compound	Empirical formula	mp, °C	IR spectra, ν, cm^{-1} (KBr)	PMR spectra ($CDCl_3$), δ, ppm (SSCC, Hz)	Mass spectra, m/z (I, %)	Yield, %
VIa	$C_{14}H_{14}N_2O_2S_2$	86...88	1596, 1578, 1480	6,54and6,42 (2H, 2s, 4-H); 2,42, 2,41, 2,38and 2,18 (12H, 4s, CH_3)	306 (14, M^+), 290 (50), 246 (100, M^+-60), 198 (14), 153 (10)	62
VId	$C_{14}H_{14}N_2O_6S_2$	203...204	1608, 1322, 1200, 1148	6,79and6,77 (2H, 2s, 4-H); 3,41and3,37 (6H, 2s, SO_2CH_3); 2,52 (6H, 2s, CH_3)	418 (5, M^+-16), 374 (100, M^+-60), 311 (30), 276 (87), 260 (38), 252 (12)	85
VIe	$C_{14}H_{18}N_2O_8S_4$	183...184	1610, 1322, 1282, 1144	6,32and6,28 (2H, 2s, 4-H); 3,92and3,91 (6H, 2s, OCH_3); 3,36 and 3,33 (6H, 2s, SO_2CH_3)	471 (2, M^+), 406 (28), 343 (13), 308 (100), 293 (15), 187 (28)	82
VIf	$C_{18}H_{22}N_2O_6S_4$	242...244	1604, 1310, 1128	7,69, 7,67, 7,52and7,48 (4H, 4d, $^3J_{4,5}=5$, 4-, 5-H); 1,40...1,43 (18H, s, *t*-Bu)	490 (10, M^+), 460 (6), 434 (100), 403 (90), 330 (55), 312 (100)	58
VIg	$C_{14}H_{12}Br_2N_2O_6S_4$	88...90	1602, 1574, 1328, 1148	3,47, 3,41 (6H, 2s, SO_2CH_3); 2,50 (6H, 2s, CH_3)	577/575/573 (6, M^+-16), 533/531/529 (100, M^+-60), 435/433/431 (100)	95
VIh	$C_{14}H_{14}N_2O_6S_4$	159...161	1610, 1322, 1146	7,70, 7,16 (4H, m, $^3J_{4,5}=5$, 4-, 5-H); 3,53 (2H, q, $J=7$, CH_2); 1,46 (3H, t, $J=7$, CH_3)	434 (4, M^+), 404 (24, M^+-30), 374 (100, M^+-60), 403 (90), 312 (100)	85
VIi	$C_{14}H_{14}N_2O_{10}S_4$	281...283	1620, 1320, 1140	7,98, 7,71 (2H, 2s, 4-H); 3,41, 3,37 (6H, 2s, SO_2CH_3); 2,52 (6H, 2s, CH_3)	532 (8, M^+-30), 502 (100, M^+-60), 438 (40), 296 (48), 235 (80)	90
VIj	$C_{14}H_{12}Br_2N_2O_2S_4$	143...145	1600, 1556, 1450	2,42, 2,38 (6H, 2s, SCH_3); 2,30, 2,27 (6H, 2s, CH_3)	530/528/526 (63, M^+), 470/468/466 (100, M^+-60), 439/437/435 (31)	80

*Compounds VIa and VIj were recrystallized from methanol; residue from ethanol.

thienylhydroxamic acid VII, the product of a 1,3-addition of water by the usual mechanism involving protonation at the oxygen atom of the nitrile oxide group.



In this connection it was of interest to trace the path of the transformations of nitrile oxides Ib and Id under the action of aprotic acids, BF_3 etherate in particular. It is known that, in the case of aromatic nitrile oxides, this can lead to the formation of isomeric, furoxane dimers B and C as well as isomer D, depending on the structure of the nitrile oxide, the amount of catalyst, and the coordinating strength of the solvent [8, 9].

In the reaction of nitrile oxide Id with an equimolar or excess amount of BF_3 etherate in ether (with a small addition of CH_2Cl_2 for better solubility) at 20°C, the sole product is furoxane VId. Such a result is evidence that, in this case, the dimerization to furoxane goes more rapidly than the formation and subsequent transformation of complex A into isomer B. Possibly this is related to the lesser coordinating ability of the oxygen atom in nitrile oxide Id compared to that of the oxygen atom in the ether. The catalytic effect of a Lewis acid is manifested in the fact that the dimerization to furoxane goes readily without heating.

The reaction was run in methylene chloride or benzene, solvents that do not coordinate the Lewis acid, at 20°C and by heating with excess catalyst. In all cases, the major reaction product, under conditions that according to [8] call for the formation of dioxadiazine C or isocyanate D, proved to be 1,2,4-oxadiazol-4-N-oxide (VIII). Its structure was confirmed by IR, PMR, and mass spectral data. The most intense peak (100%) in the mass spectrum of oxadiazole VIII corresponds to a fragment with m/z 203 (RCO). This is a characteristic feature of this structure, in contrast to the isomeric furoxanes and dioxadiazines [9]. It is interesting to note that oxadiazole VIII does not form a type B complex on treatment with BF_3 etherate, indicating the weak coordinating ability of the oxygen atom in this structure.

Trimethyl-substituted nitrile oxide Ib differs markedly in its behavior from Id under similar conditions. On reaction with BF_3 etherate in benzene (or CH_2Cl_2) at 20°C, a mixture of products that is difficult to separate is formed containing, according to TLC data, the corresponding isocyanate D.

Thus, the data obtained support the idea that the electronic influence of substituents in neighboring positions to the nitrile oxide group is a basic factor in determining the path of both thermal and catalytic transformations of substituted nitrile oxides of the thiophene series.

EXPERIMENTAL

The IR spectra were taken on Specord-275 and UR-20 instruments and the PMR spectra on Bruker WM-250 (250 MHz) and Jeol FX-90 Q (90 MHz) instruments. The mass spectra were obtained on Varian MAT-CH-6 and MAT-311-A spectrometers at an ionization voltage of 70 eV with direct introduction of the substance into the ion source.

The characteristics of new substances are given in Tables 1 and 2. The elemental analyses agreed with the calculated values.

N-(Alkylthienyl)-N'-phenylurea (IVb, c and V). A solution of 0.5 mmole of nitrile oxide Ib, c [3] or II [3] in benzene was boiled for 12 h (3 h in toluene). One mmole of $C_6H_5NH_2$ was added to the hot solution and allowed to stand for 12 h at 20°. The precipitate of mixed ureas that forms was filtered off and washed with cold C_6H_6, and recrystallized from CH_3COOH.

N-(2,4,5-Trimethylthienyl-3)-N'-phenylurea (IVb). $C_6H_5NH_2$ (0.2 mmole) was added to a mixture of 0.1 mmole of nitrile oxide Ib in 10 ml of C_6H_6 and 0.01 mmole of CF_3COOH over a period of 20 min at 20°C and allowed to stand for 12 h at 20°C. The crystals that precipitate were filtered off to obtain urea IVb in 90% yield.

Substituted 4,5-Bis(thienyl)furoxanes (VId-j). 0.5 mmole of nitrile oxides Id-j (0.5 mmole) was boiled for 6 h (12 h for If) in 50 ml of C_6H_6 (3 h in toluene for Ig). The solvent was distilled off under vacuum, and the residue recrystallized.

N-(2,5-Dimethyl-3-thienyl)-N'-phenylurea (IVa) and 4,5-Bis-(2,5-dimethyl-3-thienyl)furoxane (VIa). Nitrile oxide Ia (0.5 mmole) was boiled [3] in 50 ml of C_6H_6, and 1 mmole of $C_6H_5NH_2$ added over a 6-h period, and allowed to stand for 12 h at 20°C. The deposit of urea IVa was filtered off and washed with C_6H_6 and recrystallized. The mother liquor was washed with 10% HCl, then with water, and dried with Na_2SO_4. The solvent was distilled off under vacuum, the residue chromatographed on a column with L (40/100) silica gel (1:1 hexane/ethyl acetate), and recrystallized from CH_3OH to obtain furoxane VIa.

By a similar procedure we obtained **N-(5-methyl-4-bromo-2-methylthio-3-thienyl)-N'-phenylurea (IVj) and 4,5-bis(5-methyl-4-bromo-2-methylthio-3-thienyl)furoxane (VIj).**

2-Methylsulfonyl-5-methyl-3-thienylhydroxamic Acid (VII, $C_7H_9O_4NS_2$). To 0.5 mmole of nitrile oxide Id [10] in 50 ml of C_6H_6, was added 0.05 mmole of CF_3COOH and allowed to stand for 48 h at 20°C. Then 1 mmole of $C_6H_5NH_2$ was added and allowed to stand for 24 h at 20°C. The mixture was washed with dilute HCl, then with water, and then dried with Na_2SO_4. The solvent was distilled off, the residue washed with $CHCl_3$ (2 × 20 ml), and dried to obtain 3-thienylhydroxamic acid VII, T_{mp} 165-170°C. IR spectrum (KBr): 3290 (OH), 3190 (OH), 1643 (CO), 1560, 1520, 1300, 1155 cm^{-1} (SO_2). Mass spectrum, m/z (I, %): 235 (10, M^+), 203 (100, M – NHOH). PMR spectrum ($CDCl_3$): 2.58 (3H, s, CH_3), 3.50 (3H, s, SO_2CH_2), 7.12 (1H, s, 4-H), 8.65 (1H, broad s, NH), 11.0 ppm (1H, broad s, OH).

4,5-Bis(2-methylsulfonyl-5-methylthionyl-3)furoxane (VId). 0.2 ml (1.5 mmole) of $BF_3 \cdot Et_2O$ was added to a solution of 0.15 g (0.7 mmole) of nitrile oxide Id in a mixture of 40 ml of absolute ether and 5 ml of CH_2Cl_2 and allowed to stand for 48 h at 20°C. This was washed with water until neutral and the organic layer separated and dried with Na_2SO_4. The solvent was distilled off under vacuum, and the residue recrystallized from MeOH to obtain 0.095 g (67%) of furoxane VId.

3,5-Bis(2-methylsulfonyl-5-methylthienyl-3)-1,2,4-oxadiazole-4-N-oxide (VIII, $C_{14}H_{14}N_2O_6S_4$). A. 0.1 ml (0.8 mmole) of $BF_3 \cdot Et_2O$ was added to a solution of 0.07 g (0.3 mmole) of nitrile oxide Id in 3 ml of CH_2Cl_2 and boiled for 1 h and then treated as described above for furoxane VId. After distilling off the solvent, the residue was recrystallized from alcohol to obtain 0.05 g (70%) of compound VII, T_{mp} 235-239°C. IR spectrum (KBr): 1592, 1552, 1310, 1142 cm^{-1} (SO_2). Mass spectrum, m/z (I, %): 434 (1.5), 418 (56), 404 (6), 311 (8), 275 (53), 217 (60, RCNO), 203 (100, RCO). PMR spectrum ($CDCl_3$), δ: 2.60, 2.63 (6H, 2s, CH_3), 3.62 (6H, s, CH_3SO_2, 7.45 and 7.53 ppm (2H, s, 4-H).

B. Obtained from nitrile oxide Id and $BF_3 \cdot Et_2O$ at 20°C in C_6H_6 in 20 h. Yield 69%.

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