Reactions of (pyrrol-1-yl)furazans with electrophilic reagents*

A. B. Sheremetev, S. M. Konkina, and D. E. Dmitriev*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: sab@ioc.ac.ru

The behavior of (pyrrol-1-yl)furazans in electrophilic substitution reactions (halogenation, nitration, and acylation) was studied. The presence of the furazan ring substantially did not affect the regioselectivity of the reactions but it prevented replacement of all the hydrogen atoms in the pyrrole ring by electrophiles.

Key words: furazans, pyrroles, nitration, chlorination, bromination, formylation.

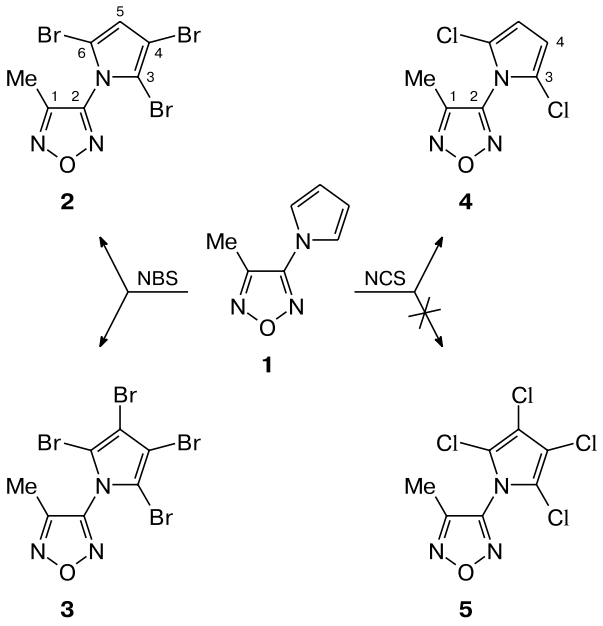
Being a strong electron acceptor, the furazan ring does not tend to conjugate with substituents.[1,2] As a result, nitration of 3-phenyl-4-R-furazans gives a mixture of three possible mononitrophenyl regioisomers, the *para*-isomer being dominant.[3—6] In bromination of the same substrates, the Br atom also goes to the *para*-position of the phenyl substituent.[7] Thus, the weak mesomeric effect of the furazan ring surpasses its electron-withdrawing effect during an electrophilic attack on the attached benzene ring. We found it interesting to examine the effect of the furazan ring on the reactivity of the attached heteroaromatic rings toward electrophilic reagents.

Earlier,[8,9] we have shown that treatment of 3-amino-4-R-furazans with 2,5-dimethoxytetrahydrofuran in boiling acetic acid is a general route to (pyrrol-1-yl)furazans. Obviously, the presence of the furazanyl substituent at the N atom of the pyrrole ring should affect the reactivity of the pyrrole part of the molecule. The present study is concerned with the specific behavior of (pyrrol-1-yl)furazans in reactions with various electrophilic reagents.

Pyrrole and its *N*-substituted derivatives are known to be easily and exhaustively brominated. Partially brominated products can be obtained only at low temperatures and under deficiency of a brominating agent.[10—15] The same is usually true for the synthesis of polychloropyrroles.[11]

We studied a reaction of 3-methyl-4-(pyrrol-1-yl)furazan (**1**) with *N*-bromosuccinimide (NBS) in glyme (Scheme 1). Unexpectedly, the reaction stopped after only three Br atoms had been introduced into the pyrrole ring. Starting at −30 °C and raising the reaction temperature to ~20 °C, we isolated 3-methyl-4-(2,3,5-tribromopyrrol-1-yl)furazan (**2**) in ~82% yield. Mixing the reagents at 20 °C or conducting the reaction at a higher temperature resulted in a lower yield of compound **2** and considerable resinification. When compound **1** was treated with an excess of NBS (5 equiv.) in trifluoroacetic acid (−30 °C → 20 °C) for 48 h, the reaction mixture contained tetrabromide **3** (GC-MS data). However, we failed to isolate this derivative. The major product was again compound **2** (~75%). It is known[11,12] that polybromopyrroles can act as brominating reagents. Apparently, one of the Br atoms in compound **3**, which is additionally activated by the furazan ring, is readily exchanged for an H atom when in contact with solvents or moisture during the workup of the reaction mixture.

Scheme 1



* Dedicated to Academician V. A. Tartakovsky on the occasion of his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1516—1520, August, 2007.

According to literature data,[16] the methyl group at the furazan ring can be monobrominated under the action of NBS. However, a NMR study revealed that the methyl group in compound **1** is not brominated in our experiments.

Chlorination of compound **1** with *N*-chlorosuccinimide (NCS, 4 mol.) in glyme or THF was less efficient. 2,5-Dichloropyrrole **4** was obtained as the sole product in ~77% yield (see Scheme 1). The formation of the 2,5-isomer was confirmed by spectroscopic methods and agrees with the usual reaction pathway.[11,17] It should be noted that the reaction in boiling THF gave a complex mixture of inseparable products. Chlorination in trifluoroacetic acid was accompanied by strong resinification. Tetrachloride **5** was not detected even by GC-MS. As in bromination, the methyl group of compound **1** was not chlorinated, although this process is possible under similar conditions.[18,19]

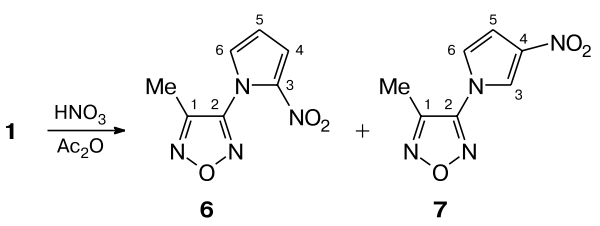
Iodination of compound **1** in acetic acid with the $KI—H_2O_2$ system did not occur at low temperature; heating resulted in resinification.

Thus, the pyrrole ring containing the furazanyl substituent at the N atom is less reactive in electrophilic halogenation.

Usually, the pyrrole ring easily undergoes electrophilic nitration leading to mono- to tetranitro derivatives.[20] At low temperature (−40 to −10 °C), *N*-substituted pyrrole can be mononitrated to give a mixture of 2- and 3-nitro products, regardless of the electronic nature of the substituent at the ring N atom. For instance, treatment of 1-methylpyrrole with HNO_3 in acetic anhydride at −30 °C mainly yields the 2-nitro isomer (the 2-nitro/3-nitro ratio was ~1.5 : 1).[21,22] The opposite pattern was observed for 1-arylpyrroles: the ratio of the 3-nitro/2-nitro isomers was ~2 : 1.[23—25]

Nitration of compound **1** at −30 °C with a mixture of 100% HNO_3 and Ac_2O also yielded two mononitrated regioisomers (Scheme 2), the reaction being accompanied by appreciable resinification. Separation of the reaction mixture by column chromatography gave 2-nitro isomer **6** (43%) and 3-nitro isomer **7** (16%); *i.e.*, the furazan ring as a substituent influences like alkyl (incapable of conjugation) rather than aryl groups.

Scheme 2



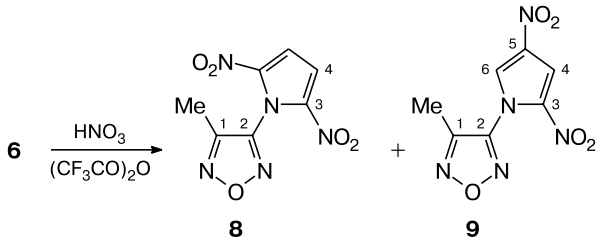
We employed ^1H and ^{13}C NMR spectroscopy (see Experimental) traditionally used to identify the resulting nitro regioisomers (see Refs 24—28). It should be noted that the observed chemical shifts agree well with the calculated ones.

We discovered that the signal for the 2-nitro isomer is shifted upfield in the ^{14}N NMR spectrum ($\delta(^{14}N)$ −27.6 *vs.* −18.7 for the 3-nitro isomer). This difference can be used for analytical purposes.

At −15 °C, nitration of a 1-substituted pyrrole containing the electron-withdrawing CF_2CF_2H group with an $HNO_3—H_2SO_4$ system gives only 2,4-dinitro product.[15] At the same time, nitration of 1-methylpyrrole at 20 °C with $HNO_3—Ac_2O$ produces a mixture of 2,3-, 2,4-, 2,5-, and 3,4-dinitro isomers with the ratio 5 : 74 : 10 : 6 in a total yield of 78%.[26] Thus, the 2,4-dinitro isomer is again the major reaction product. This regioisomer is also dominant in nitration of both 1-methyl-2-nitropyrrole and 1-methyl-3-nitropyrrole with $HNO_3—Ac_2O$ at −30 °C; the formation of nitration by-products is minimized in this case.[22]

Also we used stepwise nitration, which is more selective. Treatment of the 2-nitro isomer **6** with a mixture of nitric acid and trifluoroacetic anhydride at −30 °C afforded two dinitro products highly contaminated by parallel oxidative processes. Separation of the mixture by column chromatography gave 2,5- and 2,4-dinitropyrroles **8** and **9** in 19 and ~24% yields, respectively; *i.e.*, the isomers were obtained in approximately equal amounts (Scheme 3). Therefore, the presence of the furazanyl substituent at the N atom of the pyrrole ring changes the regiodirection of the nitration.

Scheme 3



The structures of the isomers **8** and **9** were proved by ^1H and ^{13}C NMR spectroscopy and a comparison with literature[26] and calculated data. For instance, the coupling constant $J_{4,6}$ = 2.2 Hz, which is typical of 2,4-dinitro isomers,[26—28] was observed for compound **9**.

The ^{14}N NMR spectrum of isomer **8** shows a signal at δ −31.6 ($C(3)NO_2$), while for 2,4-dinitro derivative **9**, two signals appear at δ −24.5 ($C(5)NO_2$) and −30.9 ($C(3)NO_2$). The positions of these signals correlate with the aforementioned tendency.

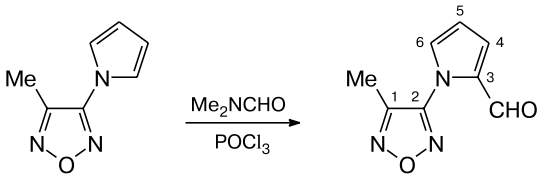
Interestingly, the nitration of the other mononitro isomer **7** under the same conditions proceeded more smoothly and regioselectively to give only 2,4-dinitro isomer **9** in ~70% yield. Isomer **7** behaves like 1-methyl-3-nitropyrrole, which is also nitrated to a 2,4-dinitro derivative (79%).[22]

The IR spectra of all the nitro derivatives obtained show bands at 1530 and 1350 cm^{-1} characteristic of nitro compounds.[29] The mass spectra of all the compounds contain an intense molecular ion peak $[M]^+$. Fragmentation starts with decomposition of the furazan ring (*via* liberation of NO) followed by elimination of the nitro group.

Unlike mononitro derivatives of *N*-methylpyrroles, which are easily brominated with NBS,[27,30] neither of the mononitro isomers (**6** or **7**) was halogenated under the action of NCS or NBS in THF at room temperature; in a boiling solvent, the reaction mixture underwent slow resinification.

The efficient Vilsmeier—Haack formylation of pyrroles with a $POCl_3$—DMF complex usually gives a mixture of two isomeric formylpyrroles, the 2-isomer being dominant.[31] Heating of compound **1** with the Vilsmeier complex in chloroform for 3.5 h resulted in considerable resinification. We isolated only 4-(2-formylpyrrol-1-yl)-3-methylfurazan (**10**) (~30%) (Scheme 4); its spectroscopic characteristics are typical of the 2-regioisomer.[32]

Scheme 4



1 **10**

To sum up, the presence of the furazanyl substituent at the N atom of the pyrrole ring substantially does not change the direction of the attack of electrophilic reagents, yet preventing exhaustive replacement of the hydrogen atoms of the pyrrole ring.

Experimental

Melting points were determined on a Gallenkamp melting unit and are given uncorrected. IR spectra were recorded on a Specord IR-75 spectrometer in KBr pellets for solids and in thin films for liquids. Natural-abundance ^1H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.7, and 21.5 MHz, respectively). Chemical shifts in the ^{14}N NMR spectra are given on the δ scale with nitromethane as the external standard. The course of the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates. For preparative chromatography, SiO_2 40/100 was used. The starting 3-methyl-4-pyrrolylfurazan **1** was prepared according to a known procedure.[8]

3-Methyl-4-(2,3,5-tribromopyrrol-1-yl)furazan (2). *N*-Bromosuccinimide (1.43 g, 8 mmol) was added in small portions at −30 °C to a solution of compound **1** (0.3 g, 2 mmol) in glyme (35 mL). The resulting mixture was stirred at −30 °C for 1.5 h and then allowed to warm to ambient temperature. The suspension was concentrated under reduced pressure. The residue was treated with CCl_4 (20 mL) and the precipitate of succinimide was filtered off. The solution was passed through a short column of silica gel and concentrated to a light yellow oil that crystallized in prolonged storage. The yield of compound **2** was 0.63 g (82%). Found (%): C, 21.82; H, 1.06; N, 10.85. $C_7H_4Br_3N_3O$ (385.84). Calculated (%): C, 21.79; H, 1.04; N, 10.89. ^1H NMR ($CDCl_3$), δ: 2.30 (s, 3 H, Me); 6.50 (s, 1 H, C(5)H). ^{13}C NMR ($CDCl_3$), δ: 7.6 (Me); 102.7 (C(3)); 103.1 (C(4)); 104.4 (C(5)); 116.6 (C(6)); 149.7 (C(1)); 150.4 (C(2)). IR, ν/cm^{-1}: 3136, 1576, 1524, 1440, 1392, 1296, 1280, 1044, 944, 900, 853, 788. MS, *m/z*: 385 $[M]^+$.

3-(2,5-Dichloropyrrol-1-yl)-4-methylfurazan (4). *N*-Chlorosuccinimide (2.1 g, 16 mmol) was added at −30 °C to a stirred solution of compound **1** (0.3 g, 2 mmol) in acetonitrile (35 mL). The reaction mixture was gradually warmed to ambient temperature and stirred for an additional 24 h. The solvent was removed *in vacuo* and the residue was suspended in CCl_4 (20 mL). The precipitate of succinimide was filtered off. The solution was passed through a short column of silica gel and concentrated *in vacuo* to a light yellow oil. The yield of product **4** was 0.33 g (77%). Found (%): C, 38.59; H, 2.33; N, 19.24; Cl, 32.49. $C_7H_5Cl_2N_3O$ (218.04). Calculated (%): C, 38.56; H, 2.31; N, 19.27; Cl, 32.52. ^1H NMR ($CDCl_3$), δ: 2.32 (s, 3 H, Me); 6.24 (s, 2 H, C(4)H). ^{13}C NMR ($CDCl_3$), δ: 7.4 (Me); 109.6 (s, 2 C, C(4), C(5)); 116.4 (s, 2 C, C(3), C(6)); 148.9 (C(2)); 150.0 (C(1)). IR, ν/cm^{-1}: 2960, 1576, 1528, 1448, 1392, 1304, 1264, 1048, 928, 856, 796. MS, *m/z*: 221, 219, 217 $[M]^+$, 191, 189, 187 $[M - NO]^+$.

Nitration of 3-methyl-4-(pyrrol-1-yl)furazan (1). A mixture of 100% HNO_3 (1.83 mL, 40 mmol) and acetic anhydride (5 mL) was added dropwise at −5 to 0 °C to a stirred solution of compound **1** (5.0 g, 33.5 mmol) in acetic anhydride (13.5 mL). The reaction mixture was allowed to warm to ambient temperature and poured onto ice (50 g). The product was extracted from the resulting emulsion with CH_2Cl_2 (3×35 mL). The combined extracts were washed with water (3×20 mL), dried over $MgSO_4$, and concentrated. The residue was chromatographed on SiO_2 with CCl_4—$CHCl_3$ (1 : 2) as an eluent.

First fraction. **3-Methyl-4-(2-nitropyrrol-1-yl)furazan (6).** The yield was 2.48 g (43%), light yellow crystals, m.p. 83.5—86 °C. Found (%): C, 43.36; H, 3.13; N, 28.83. $C_7H_6N_4O_3$ (194.15). Calculated (%): C, 43.31; H, 3.11; N, 28.86. ^1H NMR ($CDCl_3$), δ: 2.30 (s, 3 H, Me); 6.55 (dd, 1 H, C(5)H, J = 2.2 Hz, J = 1.7 Hz); 7.05 (dd, 1 H, C(6)H, J = 1.7 Hz, J = 1.3 Hz), 7.45 (dd, 1 H, C(4)H, J = 2.2 Hz, J = 1.3 Hz). ^{13}C NMR, δ: 7.7 (Me); 111.7 (C(5)); 116.0 (C(4)); 130.2 (C(6)); 137.9 (C(3)); 149.4 (C(1)); 151.9 (C(2)). ^{14}N NMR (acetone-d_6), δ: −27.6 ($\Delta\nu_{1/2}$ = 75 Hz, NO_2). IR, ν/cm^{-1}: 3136, 1584, 1572, 1540, 1496, 1452, 1360, 1328, 1320, 1288, 1168, 1100, 1048, 1032, 976. MS, *m/z* (I_{rel} (%)): 194 $[M]^+$ (8), 167, 164 $[M - NO]^+$ (11), 149 $[MH - NO_2]^+$ (100).

Second fraction. **3-Methyl-4-(3-nitropyrrol-1-yl)furazan (7).** The yield was 0.94 g (16%), green-yellow crystals, m.p. 59—64 °C. Found (%): C, 43.33; H, 3.12; N, 28.87. $C_7H_6N_4O_3$ (194.15). Calculated (%): C, 43.31; H, 3.11; N, 28.86. ^{1}H NMR ($CDCl_3$), δ: 2.53 (s, 3 H, Me); 6.85 (d, 1 H, C(6)H, J = 1.6 Hz); 7.12 (dd, 1 H, C(5)H, J = 1.6 Hz, J = 1.9 Hz); 7.45 (d, 1 H, C(3)H, J = 1.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.0 (Me); 107.9 (C(5)); 119.8 (C(3)); 121.1 (C(6)); 139.7 (C(4)); 144.8 (C(1)); 150.9 (C(2)). ^{14}N NMR ($CDCl_3$), δ: −18.7 ($\Delta\nu_{1/2}$ = 83 Hz, NO_2). IR, ν/cm^{-1}: 3160, 3128, 3112, 1624, 1592, 1544, 1520, 1496, 1392, 1376, 1296, 1232, 1176, 1080, 1048, 928, 888, 824. MS, m/z (I_{rel} (%)): 194 $[M]^+$ (100), 164 $[M - NO]^+$ (18).

(Dinitropyrrol-1-yl)furazans 8 and 9. A solution of 3-methyl-4-(2-nitropyrrol-1-yl)furazan (**6**) (0.35 g, 0.0018 mol) in a mixture of trifluoroacetic anhydride (1 mL) and CH_2Cl_2 (5 mL) was added dropwise at −30 °C to a stirred solution of 100% HNO_3 (0.13 mL, 0.19 g, 0.003 mol) and trifluoroacetic anhydride (3 mL, 1.26 g, 0.006 mol) in CH_2Cl_2 (5 mL). The dropping rate was such that the temperature was no higher than −25 °C (cooling with a dry ice/CCl_4 bath). The reaction mixture was allowed to warm to ambient temperature and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (30 mL), washed with water (3×20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting mixture (0.21 g) of regioisomers **8** and **9** was separated by column chromatography.

First fraction. **3-(2,5-Dinitropyrrol-1-yl)-4-methylfurazan (8).** The yield was 19%, an orange oil. Found (%): C, 35.20; H, 2.13; N, 29.26. $C_7H_5N_5O_5$ (239.15). Calculated (%): C, 35.16; H, 2.11; N, 29.28. ^{1}H NMR ($CDCl_3$), δ: 2.42 (s, 3 H, Me); 7.43 (s, 2 H, C(4)H). ^{13}C NMR ($CDCl_3$), δ: 7.1 (Me); 112.3 (s, 2 C, C(4)); 139.0 (s, 2 C, C(3)); 149.0 (C(2)); 149.8 (C(1)). ^{14}N NMR ($CDCl_3$), δ: −31.6 ($\Delta\nu_{1/2}$ = 50 Hz, NO_2). MS, m/z (I_{rel} (%)): 239 $[M]^+$ (100), 209 $[M - NO]^+$ (10), 193 $[M - NO_2]^+$ (4), 163 $[M - NO - NO_2]^+$ (15), 151, 140.

Second fraction. **3-(2,4-Dinitropyrrol-1-yl)-4-methylfurazan (9).** The yield was 24%, yellow crystals, m.p. 85—87 °C. Found (%): C, 35.17; H, 2.09; N, 29.24. $C_7H_5N_5O_5$ (239.15). Calculated (%): C, 35.16; H, 2.11; N, 29.28. ^{1}H NMR ($CDCl_3$), δ: 2.36 (s, 3 H, Me); 7.83 (d, 1 H, C(6)H, $J_{4,6}$ = 2.2 Hz); 7.88 (d, 1 H, C(4)H, $J_{4,6}$ = 2.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 7.7 (Me); 109.1 (C(4)); 126.3 (C(6)); 136.3 (C(3)); 136.9 (C(5)); 149.2 (C(1)); 150.7 (C(2)). ^{14}N NMR ($CDCl_3$), δ: −24.5 ($\Delta\nu_{1/2}$ = 66 Hz, C(5)NO_2); −30.9 ($\Delta\nu_{1/2}$ = 90 Hz, C(3)NO_2). IR, ν/cm^{-1}: 3136, 1584, 1560, 1552, 1536, 1528, 1516, 1480, 1424, 1356, 1312, 1296, 1208, 1184, 1088, 1048, 984, 864, 832.

Analogous nitration of 3-methyl-4-(3-nitropyrrol-1-yl)furazan (**7**) (0.33 g, 0.0017 mol) gave compound **9** (0.28 g, 69%) identical in all characteristics with the above sample.

4-(2-Formylpyrrol-1-yl)-3-methylfurazan (10). Phosphoryl chloride (0.91 g, 0.55 mL, 0.006 mol) was added dropwise to a mixture of DMF (0.46 g, 0.006 mol) and chloroform (9 mL). The addition was accompanied by a slight exothermic effect (~5 °C). The mixture was stirred for 5 min and then compound **1** (0.45 g, 0.003 mol) was added. The resulting solution was refluxed for 3.5 h, cooled to room temperature, and poured onto ice. The organic layer was separated. Organic material from the aqueous layer was extracted with chloroform (4×10 mL). The extracts were combined with the organic layer, washed with water to a neutral reaction, and dried over $MgSO_4$. The resulting solution was passed through a column with silica gel (20 g) eluted with chloroform (150 mL). The yield was 0.16 g (30%), light beige crystals, m.p. 75—76 °C. Found (%): C, 54.30; H, 4.01; N, 23.66. $C_8H_7N_3O_2$ (177.16). Calculated (%): C, 54.24; H, 3.98; N, 23.72. ^{1}H NMR ($CDCl_3$), δ: 2.23 (s, 3 H, Me); 6.54 (dd, 1 H, C(5)H, J = 2.3 Hz, J = 1.7 Hz); 7.13 (dd, 1 H, C(4)H, J = 1.7 Hz, J = 1.1 Hz); 7.25 (dd, 1 H, C(6)H, J = 2.3 Hz, J = 1.1 Hz); 9.61 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$), δ: 7.8 (Me); 112.6 (C(5)); 125.8 (C(6)); 131.5 (C(3)); 132.8 (C(4)); 149.4 (C(1)); 152.8 (C(2)); 178.5 (CHO). IR, ν/cm^{-1}: 3112, 2928, 2848, 1652, 1584, 1528, 1456, 1356, 1288, 1240, 1056, 1040, 984. MS, m/z: 177 $[M]^+$, 147 $[M - NO]^+$.

This work was financially supported in part by the Division of Chemistry and Materials Sciences of the Russian Academy of Sciences (Program OKh-05).

References

1. A. B. Sheremetev, *Usp. Khim.*, 1999, **68**, 154 [*Russ. Chem. Rev.*, 1999, **68**, 137 (Engl. Transl.)].
2. A. B. Sheremetev, N. N. Makhova, and W. Friedrichsen, in *Adv. Heterocycl. Chem.*, Academic Press, 2001, **78**, 65.
3. F. D. Dodge, *Liebigs Ann.*, 1891, **264**, 178.
4. A. De Munno, V. Bertini, A. Menconi, and G. Denti, *Atti Soc. Tosc. Sci. Nat., Mem., Ser. A*, 1974, **81**, 334.
5. M. R. Zelenov, G. M. Frolova, S. F. Mel´nikova, and I. V. Tselinskii, *Khim. Geterotsikl. Soedin.*, 1982, **18**, 27 [*Chem. Heterocycl. Compds.*, 1982, **18**, 21 (Engl. Transl.)].
6. R. Calvino, B. Ferrarotti, A. Gasco, and A. Serafino, *J. Heterocycl. Chem.*, 1983, **20**, 1419.
7. A. De Munno, V. Bertini, P. Rasero, N. Picci, and L. Bonfanti, *Atti. Accad. Naz. Lincei*, 1978, **64**, 385.
8. A. B. Sheremetev, S. M. Konkina, I. L. Yudin, D. E. Dmitriev, B. B. Averkiev, and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1337 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1413].
9. A. B. Sheremetev, Yu. L. Shamshina, D. E. Dmitriev, D. V. Lyubetskii, and M. Yu. Antipin, *Heteroatom Chem.*, 2004, **15**, 199.
10. M. M. El´chaninov, A. M. Simonov, and L. Ya. Oleinikova, *Khim. Geterotsikl. Soedin.*, 1980, 71 [*Chem. Heterocycl. Compds.*, 1980, **16**, 59 (Engl. Transl.)].
11. H. M. Gilow and D. E. Burton, *J. Org. Chem.*, 1981, **46**, 2221.
12. E. Baum, L. I. Belen´kii, V. G. Kul´nevich, and T. E. Goldovskaya, *Khim. Geterotsikl. Soedin.*, 1982, 662 [*Chem. Heterocycl. Compds.*, 1982, **18**, 499 (Engl. Transl.)].
13. G. W. Gribble, D. H. Blank, and J. P. Jasinski, *Chem. Commun.*, 1999, 2195.
14. G. W. Gribble, *Environ. Sci. Pollut. Res.*, 2000, **7**, 37.
15. L. M. Yagupol´skii, T. M. Sokolenko, and K. I. Petko, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 781 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 796].
16. R. A. Kenley, C. D. Bedford, O. D. Dailey, R. A. Howd, and A. Miller, *J. Med. Chem.*, 1984, **27**, 1201.
17. I. Sircar, J. C. Hodges, J. Quin III, A. M. Bunker, R. T. Winters, J. J. Edmunds, C. R. Kostlan, C. Connolly, S. J. Kesten, J. M. Hamby, J. C. Topliss, J. A. Keiser, and R. L. Panek, *J. Med. Chem.*, 1993, **36**, 2253.
18. I. V. Vigalok, A. V. Ostrovskaya, N. V. Svetlakov, T. V. Zykova, and N. A. Zhikhareva, *Khim. Geterotsikl. Soedin.*,

1977, **13**, 30 [*Chem. Heterocycl. Compds.*, 1977, **13**, 25 (Engl. Transl.)].
19. O. A. Ivanova, E. B. Averina, T. S. Kuznetsova, and N. S. Zefirov, *Khim. Geterotsikl. Soedin.*, 2000, **36**, 1251 [*Chem. Heterocycl. Compds.*, 2000, **36**, 1091 (Engl. Transl.)].
20. J. H. Boyer, *Nitroazoles. The C-Nitro Derivatives of Five-Membered N- and N,O-Heterocycles*, VCH, Weinheim, Federal Republic of Germany, 1985, 1.
21. H. J. Anderson, *Can. J. Chem.*, 1957, **35**, 22.
22. E. N. Safonova, V. M. Belikov, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1959, 1307 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1959, **8**, 1258].
23. J. Dhont and J. P. Wibaut, *Recl. Trav. Chim. Pays-Bas*, 1943, **62**, 177.
24. D. Korakas and G. Varvounis, *J. Heterocycl. Chem.*, 1996, **33**, 611.
25. J. Cobb, I. N. Demetropoulos, D. Korakas, S. Skoulika, and G. Varvounis, *Tetrahedron*, 1996, **52**, 4485.
26. L. Grehn, *Chem. Scripta*, 1978—79, **13**, 67.
27. L. Grehn, *Chem. Scripta*, 1980, **16**, 72.
28. L. Grehn, *Chem. Scripta*, 1980, **16**, 85.
29. V. A. Shlyapochnikov, *Kolebatel´nye spektry alifaticheskikh nitrosoedinenii* [*Vibrational Spectra of Aliphatic Nitro Compounds*], Nauka, Moscow, 1989 (in Russian).
30. G. Cirrincione, A. M. Almerico, A. Passannanti, P. Diana, and F. Mingoia, *Synthesis*, 1997, 1169.
31. B. A. Trofimov, *Usp. Khim.*, 1989, **58**, 1703 [*Russ. Chem. Rev.*, 1989, **58**, 967 (Engl. Transl.)].
32. M. del K. Pina, V. A. Budylin, M. Rodriguez, and J. G. Bundel, *Khim. Geterotsikl. Soedin.*, 1989, 324 [*Chem. Heterocycl. Compds.*, 1989, **25**, 268 (Engl. Transl.)].

Received June 22, 2007;
in revised form July 25, 2007