Oximes as Intermediates or Final Products in Reactions of Nitroheteroarenes with Nucleophiles in the Presence of Sodium Methoxide-Methanol System

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Received October 29, 2002

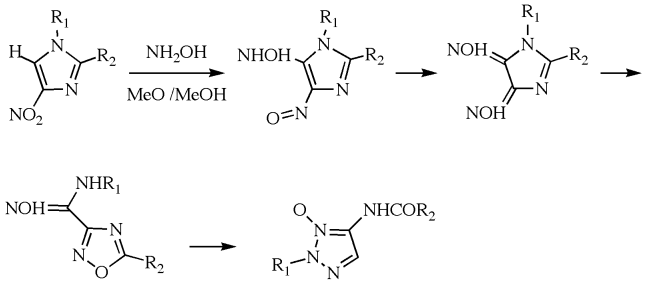
It has been shown that reactions of 4-nitroimidazoles and some other nitroaromatic systems with phenylacetonitrile in the presence of sodium methoxide in methanol lead to the reduction of the nitro to nitroso group and to the nucleophilic displacement of hydrogen atom at the ring by the respective carbanion followed by tautomerization of the nitroso compound to an oxime. Similar reactions of 4-nitroimidazoles with such nucleophiles as anions generated from 4-amino-1,2,4-triazole occur with the ring transformation of imidazole into 1,2,4-oxadiazole derivatives sometimes undergoing further processes in the reaction medium. Structures of some products have been confirmed by X-ray diffraction analysis.

J. Heterocyclic Chem., **40**, 523 (2003).

Introduction.

Nitroimidazoles due to their wide biological activity and several practical applications have been of great interest for a long time. Studying reactions of 1-aryl-4-nitroimidazoles with hydroxylamine in methanol in the presence of sodium methoxide we have observed a very unique ring transformation of the starting materials into 1,2,3-triazole 1-oxide derivatives [1]. Some reactions of 4-nitroimidazoles with other nucleophiles have also occurred with the ring transformation leading this time to 1,2,4-oxadiazole derivatives [1-4]. Based on these observations we postulated [4] a reaction mechanism beginning from nucleophilic attack on carbon 5 of 4-nitroimidazole followed by reduction of nitro to nitroso group. In the next step oxime formation occurs followed by rearrangement into the oxadiazole, which may undergo further reactions to afford 1,2,3-triazole 1-oxide derivatives (Scheme 1) [1] or acyclic products [4].

Scheme 1



The formation of nitroso compounds and oximes in the studied reactions has not been proved till now. In contrast to that we have shown that the hydride and electrochemical reductions of 1-aryl-4-nitroimidazoles lead to the formation of stable oximes of imidazolones or imidazolidinones [5 - 7].

Davis and Pizzini [8] investigated a reaction of phenylacetonitrile with some nitroarenes in boiling methanol in the presence of sodium hydroxide and observed a displacement of the hydrogen atom and reduction of the nitroarenes (*e.g.* 1-nitronaphthalene) to the respective oximes. Later on Wróbel [9] showed that a similar reaction carried out in aprotic solvents like DMF and in the presence of DBU and $MgCl_2$ afforded the naphthoisoxazole in a moderate yield. It may be assumed that, in reactions occurring in protic solvents, the nucleophilic carbanion

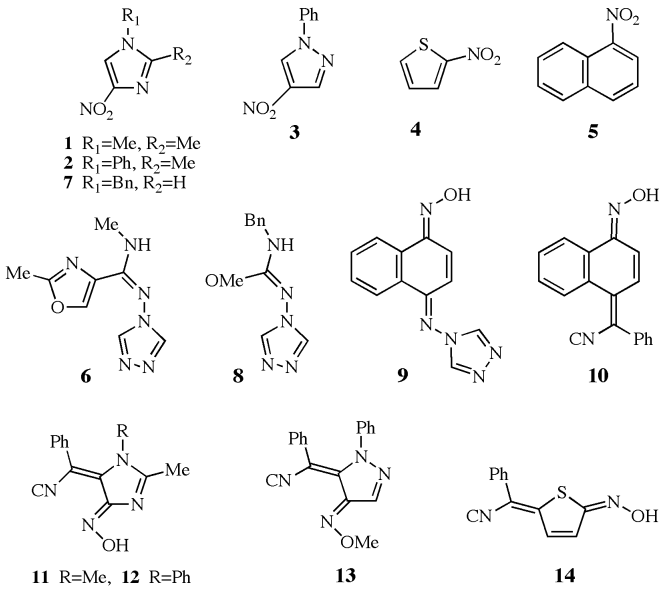


Figure 1. Structures and numbers of compounds investigated.

generated from phenylacetonitrile played a role similar to the hydride anion in the hydride reduction of nitroazoles. Therefore in this work we decided to investigate reactions of 4-nitroimidazoles **1**, **2** (Figure 1) with phenylacetonitrile carbanion, aiming to obtain respective oximes. The reactions were carried out in methanol in the presence of sodium methoxide at *ca*. 25 °C for 48 hours; therefore, the conditions were close to those that we used earlier [1 - 4].

For a comparison, we also looked for product structures of similar reactions of phenylacetonitrile carbanion with 4-nitro-1-phenylpyrazole (**3**), 2-nitrothiophene (**4**), and 1-nitronaphthalene (**5**). In the case of the latter three starting nitrocompounds, further transformations of oximes would be much less likely than in the case of nitroimidazoles.

Results and Discussion.

At the beginning of this work, in order to undoubtedly prove a formation of oxadiazoles in reactions of 4-nitroimidazoles with some nucleophiles, we obtained a monocrystal of the respective product from 1,2-dimethyl-4-nitroimidazole (**1**) and 4-amino-1,2,4-triazole and elucidated its structure by X-ray analysis. Results of the analysis of obtained N^1-methyl-N^2-(1,2,4-triazol-4-yl)-5-methyl-1,2,4-oxadiazole (**6**) (Figure 2 and Table 1) are fully consistent with the structure proposed earlier [3].

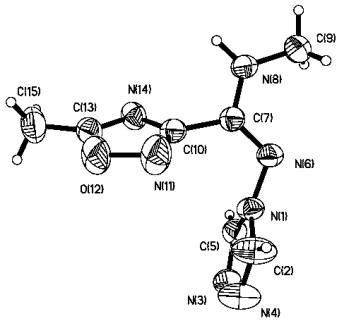


Figure 2. The projection of N^1-methyl-N^2-(1,2,4-triazol-4Ô-yl)-5-methyl-1,2,4-oxadiazole (**6**). Displacement ellipsoids are drawn at the 50% probability level [10].

Table 1

Crystal Data Collection and Refinement for N^1-Methyl-N^2-(1,2,4-triazol-4-yl)-5-methyl-1,2,4-oxadiazole (**6**)

Formula	$C_7H_9N_7O$	V	3944.5(14) Å^3
Crystal system	Orthorhombic	Z	16
Space group	Fdd2	D_{calc}	1.504 g/cm^3
a	21.564(4) Å	Collected reflections	943
b	25.840(5) Å	Independent reflections	943
c	7.0790(14) Å	Agreement factor R	0.0336

Not being able to isolate oxadiazole derivative from a similar reaction of 4-nitro-1-benzylimidazole (**7**; free position 2 of imidazole ring!) with 4-amino-1,2,4-triazole we looked for a structure of the product probably forming by a decomposition of the oxadiazole ring under reaction conditions [3]. The results of X-ray analysis (Figure 3, Table 2) confirms its structure as *N*-benzyl-*O*-methyl-*N'*-1,2,4-thriazol-4-yl)isourea (**8**) and the same supports our speculative mechanism of 4-nitroimidazole reactions with 4-amino-1,2,4-triazole in the presence of sodium methoxide-methanol system [3].

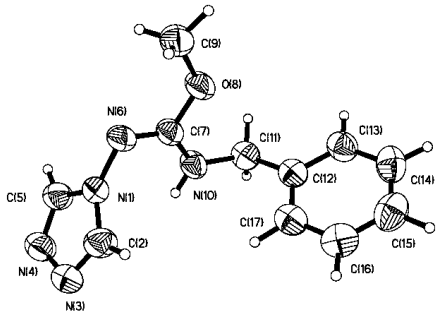


Figure 3. The projection of *N*-benzyl-*O*-methyl-*N*'-1,2,4-triazol-4-yl)isourea (**8**) structure. Displacement ellipsoids are drawn at the 50% probability level [10].

Table 2

Crystal Data Collection and Refinement for *N*-Benzyl-*O*-methyl-*N'*-1,2,4-triazol-4-yl)isourea (**8**)

Formula	$C_{11}H_{13}N_5O$	V	1185.4(4) Å^3
Crystal system	Orthorhombic	Z	4
Space group	$P2_12_12_1$	D_{calc}	1.285 g/cm^3
a	5.5020(11) Å	Collected reflections	1267
b	8.1290(16) Å	Independent reflections	1267
c	26.504(4) Å	Agreement factor R	0.0303

In contrast to the above results a reaction of nitronaphthalene **5** with 4-amino-1,2,4-triazole gave (*E*) 1-(1',2',4'-triazol-4'-yl)imino-1,4-naphtoquinone (*E*)-oxime (**9**) (Figure 4, Table 3). Also a corresponding oxime namely (*E*) 4-cyanophenylmethylene-1,4-naphthoquinone (*E*)-oxime (**10**) was obtained from a reaction of nitronaphthalene **5** with phenylacetonitrile (Figure 5, Table 4) performed under similar conditions. The structures of **9** and **10** were also confirmed by X-ray.

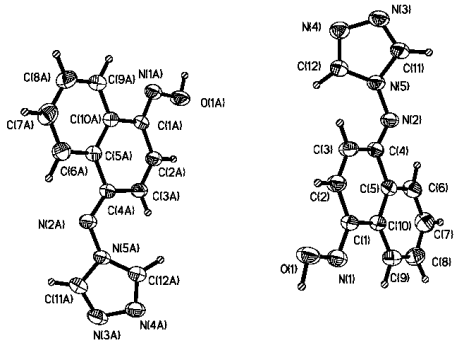


Figure 4. Crystal data collection and refinement for (*E*) 1-(1',2',4'-triazol-4'-yl)imino-1,4-naphtoquinone (*E*)-oxime (**9**) [10].

Table 3

Crystal Data Collection and Refinement for (*E*) 1-(1',2',4'-Triazol-4'-yl)imino-1,4-naphtoquinone (*E*)-oxime (**9**)

Formula	$C_{12}H_9N_5O$	V	4401.0(17) Å^3
Crystal system	Monoclinic	Z	8
Space group	C2/c	D_{calc}	1.444 g/cm^3
a	21.329(4) Å	Collected reflections	18490
b	7.666(2) Å	Independent reflections	4839
c	27.958(6) Å	Agreement factor R	0.0489
β	105.69(3)°		

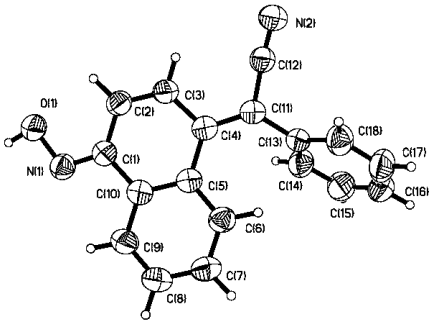


Figure 5. The projection of (*E*) 4-cyanophenylmethylene-1,4-naphthoquinone (*E*)-oxime (**10**). Displacement ellipsoids are drawn at the 50% probability level [10].

Table 4

Crystal Data Collection and Refinement for (*E*) 4-Cyanophenylmethylene-1,4-naphthoquinone (*E*)-oxime (**4**)

Formula	$C_{18}H_{12}N_2O$	V	2788.1(11) Å^3
Crystal system	Orthorhombic	Z	8
Space group	Pbca	D_{calc}	1.297 g/cm^3
a	13.666(3)Å	No. of collected reflections	2113
b	8.807(2) Å	No. independent reflections	2113
c	23.165(5) Å	Agreement factor R	0.0352

Assuming that phenylacetonitrile carbanion would be less reactive than the anion generated from 4-amino-1,2,4-triazole and that the presence of the 2-methyl group in a starting nitroimidazole would prevent, at least to some extent, attacks of nucleophiles on carbon 2, both in the starting nitroimidazole and in a product, we carried out reactions of 1-alkyl-(or aryl)-2-methyl-4-nitroimidazoles (**1**, **2**) with phenylacetonitrile in methanol in the presence of sodium methoxide at 25 °C and observed this time a formation of oximes **11**, **12** as the final products (Scheme 2, Table 5).

The oximes **11** and **12** were stable in the reaction mixture. In contrast to oximes, postulated as intermediates in reactions of 4-nitroimidazoles with several other nucleophiles [2-4], they did not rearrange to the corresponding 1,2,4-oxadiazoles even after a few days. Under similar conditions, nitropyrazole **3** reacting with phenylacetonitrile afforded methyl ether of the respective oxime **13** in low yield. Nitrothiophene **4** behaved like the 4-nitroimidazoles **1** and **2** though the nucleophilic cyanophenylmethyl anion did not attack position 3 neighboring to the one bearing the nitro group, but did attack the quasi-*para* position 5 (Table 5).

^{1}H NMR spectra analysis of **11, 12** has not brought sufficient information on the product structures, particularly stereochemical. The proposed structures for **11** and **12** are not fully aromatic and may exist in four stereoisomeric forms. To remove any doubts concerning the structures of **11** (and **12**) we succeeded in obtaining a monocrystal of **11**. Results of **11** X-ray analysis are shown below (Figure 6 and Tables 6 - 7).

The formation of *O*-methyl derivative of the expected oxime **13** from nitropyrazole **3** (Table 5, Scheme 3), under the conditions used here, seems to confirm some slightly different behavior between the nitrosoimidazoles and nitrosopyrazoles, observed also in the hydride reduction [5]. As we have already mentioned, the hydride reduction of 4-nitroimidazoles affords oximes of imidazolones or imidazolidinones. A similar reduction of 4-nitropyrazole gives 4,4'-azoxypyrazole. In both reactions, respective nitroso derivatives have been postulated as intermediates [5]. Probably the nitroso group, in the pyrazole derivatives, is more susceptible to nucleophiles than that of the imidazoles.

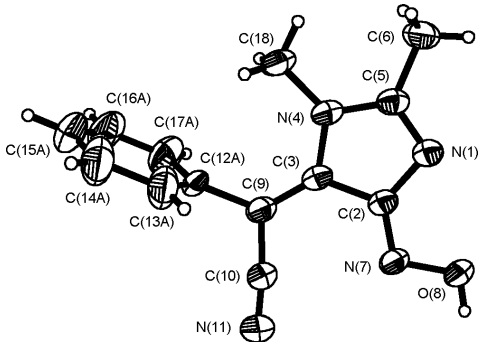


Figure 6. The projection of (*E*) 5-cyanophenylmethylene-1,2-dimethyl-4-imidazolone (*E*)-oxime (**11**) structure. Displacement ellipsoids are drawn at the 50% probability level [10].

Table 5

Results of Nitroimidazoles **1**, **2**, 4-Nitropyrazole **3** and Nitrothiophene **4** Reaction with Phenylacetonitrile in Sodium Methoxide-Methanol System

Starting material	Product	Yield [%]
1	**11**	71
2	**12** (*E*+*Z*)	87
3	**13**	28
4	**14**	62

Table 6

Crystal Data Collection and Structure Refinement for (*E*) 5-Cyanophenylmethylene-1,2-dimethyl-4-imidazolone (*E*)-oxime (**11**)

Formula	$C_{13}H_{12}N_4O$	V	607.78(9) Å^3
Crystal system	Triclinic	Z	2
Space group	*P*1	D_{calc}	1.313 g/cm^3
a	6.9126(9) Å	Collected reflections	2766
b	8.1129(3) Å	Independent reflections	2544
c	11.4568(6) Å	Agreement factor R	0.0382
α	108.249(7)°		
β	93.334(7)°		
χ	92.614(6)°		

Table 7

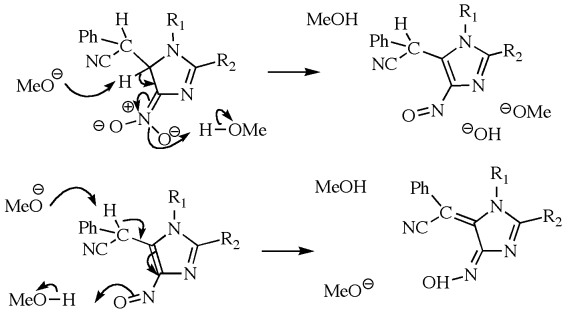
Bond Lengths [Å] and Angles [°] for **11**

Bond length		Angle	
N(1)-C(5)	1.302(1)	C(5)-N(1)-C(2)	104.5(1)
N(1)-C(2)	1.396(1)	N(7)-C(2)-N(1)	127.8(1)
C(2)-N(7)	1.291(1)	N(7)-C(2)-C(3)	122.3(1)
C(2)-C(3)	1.480(2)	N(1)-C(2)-C(3)	109.90(9)
C(3)-C(9)	1.356(2)	C(9)-C(3)-N(4)	128.3(1)

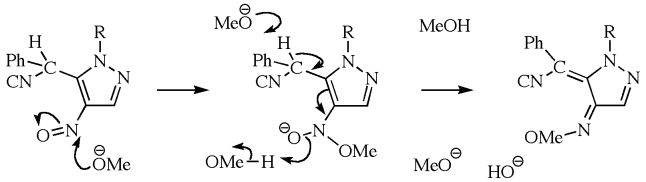
Bond lengths [Å] and angles [°] for **11**

Bond length		Angle	
C(3)-C(9)	1.356(2)	C(9)-C(3)-C(2)	129.1(1)
C(3)-N(4	1.387(1)	N(4)-C(3)-C(2)	102.68(9)
N(4)-C(5)	1.374(2)	C(5)-N(4)-C(3)	107.74(9)
N(4)-C(18)	1.458(1)	C(5)-N(4)-C(18)	124.90(1)
C(5)-C(6)	1.487(2)	C(3)-N(4)-C(18)	127.4(1)
N(7)-O(8)	1.386(1)	N(1)-C(5)-N(4)	115.2(1)
C(9)-C(10)	1.427(2)	N(1)-C(5)-C(6)	123.4(1)
C(10)-N(11)	1.142(2)	N(4)-C(5)-C(6)	121.5(1)
		C(2)-N(7)-O(8)	111.56(9)
		C(3)-C(9)-C(10)	119.38(9)
		C(3)-C(9)-C(12)	127.3(4)
		C(10)-C(9)-C(12)	113.3(4)
		C(3)-C(9)-C(12A)	127.0(3)
		C(10)-C(9)-C(12A)	113.3(3)
		N(11)-C(10)-C(9)	174.3(1)
		C(13)-C(12)-C(9)	119.1(5)
		C(17)-C(12)-C(9)	120.9(5)
		C(13A)-C(12A)-C(9)	118.4(4)
		C(17A)-C(12A)-C(9)	121.6(4)

Scheme 2



Scheme 3



Conclusion.

The results of this work prove clearly that oximes can be intermediate or final products in reactions of 4-nitroimidazoles with nucleophiles. More active nucleophiles lead to formation of oxadiazoles or products of their further transformations. Some less reactive nucleophiles like the carbanion generated from phenylacetonitrile in the presence of sodium methoxide - methanol system enables to obtain respective oximes as final products.

EXPERIMENTAL

Melting points were not corrected. NMR spectra were acquired at 300 MHz for ^{1}H NMR and 62.9 MHz for ^{13}C NMR on a Varian spectrometer with TMS as an internal standard. MS spectra were recorded using Shimadzu GCMS QP-2000 apparatus. TLC plates (Merck, silica gel 60F_{254}) were developed in UV and in iodide vapors. 2-Nitrothiophene (**4**), 1-nitronaphthalene (**5**) and solvents were commercially purchased. Starting 4-nitroimidazoles **1, 2, 7** were obtained according to the procedure published earlier by us [2]. Properties of the compounds were in accordance with those reported earlier. 4-Nitro-1-phenylpyrazole (**3**, m.p. 129-130 °C) was prepared according to [11].

Reactions of Nitrocompounds **1-5** with phenylacetonitrile (a general procedure).

Sodium (1.2 g) was dissolved in methanol (50 cm^3) and then a nitrocompound (2 mmole) was added at room temperature followed by phenylacetonitrile (4 mmole). Progress of the reaction was monitored by means of TLC (benzene: ethyl acetate, 4:1; UV). The resulting reaction mixture was acidified by concentrated hydrochloric acid to pH = 5 and evaporated under diminished pressure at 60 °C up to volume of 50 cm^3. The concentrated mixture was poured into cold water (50 cm^3) and extracted three times with chloroform. The combined extracts were dried over magnesium sulfate(VI) and the solvents were evaporated at 60 °C under slightly diminished pressure. Anhydrous diethyl ether (20 cm^3) was added to the residue and the resulting solution was kept at 0 °C for three hours. Crystals separating on cooling were collected and recrystallized from suitable solvents as indicated below.

(*E*) 4-Cyanophenylmethylene-1,4-naphthoquinone (*E*)-oxime (**10**).

This compound was obtained in 76% yield, mp 179-181 °C (methanol-water); ^{1}H NMR (ppm, dmso-d_6): δ 12.50 (s, 1H, *NOH*), 8.34-6.94 (m, 11H, *Ar*); MS 70 eV (m/e, %): M^+ 272 (28.8), 255 (1000), 227 (41.1), 201 (16.0), 100 (31.6), 52 (25.0).

Anal. Calcd. for $C_{18}H_{12}N_2O$: C, 79.35; H, 4.44; N, 10.29. Found C, 79.84; H, 4.30; N, 10.29.

5-Cyanophenylmethylene-1,2-dimethyl-4-imidazolone (*E*)-oxime (**11**).

This compound was obtained in 71% yield; mp 187 °C dec. (methanol); ^{1}H NMR (ppm, dmso-d_6): δ 11.92 (s, 1H, *NOH*), 7.46-7.42 (m, 5H, *Ph*), 2.66 (s, 3H, *N-CH$_3$*), 2.24 (s, 3H, *C-CH$_3$*); MS 70 eV (m/e, %): 239 (34.2), 223 (100.0), 208 (14.5), 141 (33.5), 127 (17.9), 57 (78.0), 52 (14.5).

Anal. Calcd. for $C_{13}H_{12}N_4O$: C, 64.98; H, 5.03; N, 23.32. Found C, 65.57; H, 5.03; N, 23.32.

5-Cyanophenylmethylene-2-methyl-1-phenyl-4-imidazolone (*E+Z*)-oxime (**12**).

This compound was obtained in 87% yield; mp 182 °C dec. (methanol-water); ^{1}H NMR (ppm, dmso-d_6): δ 12.07 (s, 1H, *NOH*), 7.07-6.92 (m, 10H, *2×Ph*), 1.99 (s, 3H, C*H$_3$*); MS 70 eV (m/e, %): 285 (80.5), 243 (27.6), 77 (100), 52 (67.5).

Anal. Calcd. for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.67; N, 18.53. Found C, 71.09; H, 4.67; N, 18.80.

5-Cyanophenylmethylen-1-phenyl-4-pyrazolone *O*-methyloxime (**13**).

This compound was obtained in 28% yield, mp 132-133 °C (methanol); ^{1}H NMR (ppm, dmso-d_6): δ 8.6-7.47 (m, 11H, *2×Ph+CH*), 4.14 (s, 3H, *OCH$_3$*); ^{13}C NMR (ppm, dmso-d_6): δ 156.87, 155.58, 147.72, 139.43, 137.09, 135.38, 130.19, 128.65, 128.49, 127.78, 127.67, 124.73, 119.45, 53.97); MS 70 eV (m/e, %): 302 (76.9), 274 (11.6), 129 (13.4), 104 (13.8), 77(100), 52 (43.0).

Anal. Calcd. for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.67; N, 18.53. Found C, 72.11; H, 4.59; N, 18.53.

5-Cyanophenylmethylene-2-thiophenone (*E*)-oxime (**14**).

This compound was obtained in 62% yield; mp 178-179 °C (lit. 188 °C [12], methanol); ^{1}H NMR (ppm, dmso-d_6): δ 13.24 (s, 1H, *NOH*), 7.54-7.47 (m, 5H, *Ph*), 7.44 (d J=7Hz, *CH*), 6.59 (d, J=7Hz, *CH*); MS 70 eV (m/e, %): M$^+$ 228 (11.2), 227 (11.9), 211 (100), 140 (19.2), 105 (11.4), 77 (17.6), 52 (21.7).

Reaction of 1-Nitronaphtalene (**5**) with 4-Amino-1,2,4-triazole.

Sodium (1.2 g) was dissolved in methanol (50 cm^3) and then **5** (2 mmole) was added at room temperature followed by 4-amino-1,2,4-triazole (2 mmole). Progress of the reaction was monitored by means of TLC (benzene: ethyl acetate, 4:1; UV). The resulting reaction mixture was acidified by concentrated hydrochloric acid to pH = 5 and evaporated under diminished pressure at 60 °C up to *ca*. 50% of the starting volume. The concentrated mixture was poured into cold water (50 cm^3) and extracted three times with chloroform. The combined extracts were dried over magnesium sulfate(VI) and the solvents were evaporated at 60 °C under slightly diminished pressure. Anhydrous diethyl ether (20 cm^3) was added to the residue and the resulting solution was kept at 0 °C for three hours. Crystals separating on cooling were collected and recrystallized from methanol-water mixture.

4-Imino(1,2,4-triazol-4-yl)-1,4-naphtoquinone oxime (**9**).

This compound was obtained in 83% yield, 276 °C dec. (methanol-water); ^{1}H NMR (ppm, dmso-d_6): δ 13.17 (s, 1H, *NOH*), 8.94 (s, 2H, *Tr-H*), 8.48 - 7.73 (m, 6H, *Ar*); MS 70 eV (m/e, %): M$^+$ 239 (98.5), 238 (14.9), 223 (36.5), 184 (17.4), 168 (19.5), 157 (40.2), 141 (42.7), 140 (100.0), 128 (30.6), 114 (35.9), 102 (44.3), 88 (14.0), 75 (17.3).

Anal. Calcd. for $C_{12}H_8N_5O$: C, 60.50; H, 3.38; N, 28.96. Found C, 60.48; H, 3.68; N, 29. 30.

X–Ray Analysis.

N^1-Methyl-*N*^{2}-(1,2,4-triazol-4-yl)-5-methyl-1,2,4-oxadiazole-3-carboxamidine (**6**).

Diffraction data were collected using MoKα radiation (0.71073 Å) on a four circle KUMA KM-4 diffractometer with a graphite monochromator at 295 K using ϖ-2θ scan. The structure was determined by means of direct methods [13] and refined by the full-matrix least squares technique. [14] Position of non–hydrogen atoms were determined using anisotropic thermal parameters. Hydrogen atom H81 (bonded with N8 atom) was found in subsequent difference Fourier maps. Rest of hydrogen atoms were introduced in their idealized positions and refined as isotropic with their thermal parameters restricted to a value of 1.2 (for CH) and 1.5 (for CH_3 and OH) times U_{eq} of their parent C atom. For all of them a riding model refinement was used (C-H bonds set to 0.96 Å and 0.93 Å for CH_3 and CH_{ar} respectively).

N-Benzyl-*O*-methyl-*N'*-(1,2,4-triazol-4-yl)isourea (**8**), 1-(1,2,4-Triazol-4-yl)imino-1,4-naphtoquinone (*E*)-oxime (**9**) and 4-Cyanophenylmethylene-1,4-naphtoquinone (*E*)-oxime (**10**).

Diffraction data were collected using MoKα radiation (0.71073 Å) on a four circle KUMA KM-4 diffractometer with a graphite monochromator at 295 K using ϖ-2θ scan. The structure was determined by means of direct methods [13] and refined by the full-matrix least squares technique. [14] Positions of non–hydrogen atoms were determined using anisotropic thermal parameters. All hydrogen atoms were found in subsequent difference Fourier maps and isotropically refined.

(*E*) 5-Cyanophenylmethylene-1,2-dimethyl-4-imidazolone (*E*)-oxime (**11**).

Diffraction data were collected using CuKα radiation (1.54178 Å) on a four circle KUMA KM-4 diffractometer with a graphite monochromator at 295 K using ϖ-2θ scan. The structure was determined by means of direct methods [13] and refined by the full-matrix least squares technique. [14] Non-hydrogen atoms, except for those in the phenyl group, were refined anisotropically. The ring in phenyl substituent was assumed to be disordered over two orientations, both fitted to regular hexagons (C-C bonds set to 1.39 Å). Their site occupation factors refined to the values of 0.452(5) and 0.548(5) for C(12) to C(17) and C(12A) to C(17A), respectively. The single bond length to the phenyl ring C(9)-C(12) (and C(9)-C(12A)) was restrained to 1.500(1) Å. Hydrogen atoms were introduced in their idealized positions and refined as isotropic with their thermal parameters restricted to a value of 1.2 (for CH) and 1.5 (for CH_3 and OH) times U_{eq} of their parent C atom. For all of them a riding model refinement was used (C-H bonds set to 0.96 Å, 0.93 Å and 0.82 Å for CH_3, CH_{ar} and OH, respectively). The final discrepancy index was R = 0.0382 [I > 2σ(I)]. Selected experimental details and crystal data are given in Tables 6 and 7. An attempt was made in order to distinguish between the two possibilities: the partially disordered mode as described above and the structure of lower symmetry. Thus, the structure was additionally solved in triclinic P1 group giving two molecules with slightly different phenyl ring orientations. Lowering of the symmetry, however, did not lead to a better result.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers: **6**: CCDC 185561; **8**: CCDC 185562; **9**: CCDC 185560; **10**: CCDC 185559; **11**: CCDC 185563. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

REFERENCES AND NOTES

[1] J. Suwiński, K. Świerczek and T. Głowiak, *Tetrahedron*, **49**, 5339 (1993).

[2] J. Suwiński, W. Pawlus, E. Salwińska and K. Świerczek, *Heterocycles*, **37**, 1511 (1994).

[3] J. Suwińskii and K. Świerczek, *Khim. Geterots. Soed*., 1214 (1996).

[4] J. Suwiński and K. Świerczek, *Khim. Geterots. Soed*., 762 (1998).

[5] J. Suwiński, P. Wagner and E. M. Holt, *Acta Cryst. C*, ***52***, 1462 (1996).

[6] J. Suwiński, P. Wagner and E. M. Holt, *Tetrahedron*, **52**, 9541 (1996).

[7] A. Tallec, R. Hazard, J. Suwiński and P. Wagner, *Polish J. Chem*., **74**, 1177 (2000).

[8] R. B. Davis and L. C. Pizzini, *J. Org. Chem*., **25**, 1884 (1960).

[9] Z. Wróbel, *Polish J. Chem*., **72**, 2384 (1998).

[10] SHELXTL ver. 5.10, Brucker AXS (2000).

[11] I. L. Finar and R. J. Hurlock, *J. Chem. Soc*., 3024 (1957).

[12] P. Fournari and T. Marey, *Bull. Soc. Chim. Fr*., 3223 (1968).

[13] G. M. Sheldrick, *Acta Cryst. A*, **46**, 467 (1990).

[14] G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures. Univ. of Göttingen: Germany (1997).