Dinitrofuroxan cycloreversion as a novel general approach for the synthesis of nitroazoles*

*L. L. Fershtat, D. V. Khakimov, and N. N. Makhova**

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: mnn@ioc.ac.ru

A novel general approach towards various nitroazoles *via* tandem process involving dinitrofuroxan cycloreversion followed by [3+2] cycloaddition of generated *in situ* nitroformonitrile oxide is developed. The reaction is promoted by addition of catalytic amounts of ionic liquids. Plausible mechanisms of the described processes based on quantum chemical calculations are proposed.

Key words: dinitrofuroxan, nitroformonitrile oxide, nitroazoles, cycloreversion, [3+2] cycloaddition, ionic liquids, catalysis, quantum chemical calculations.

1,3-Dipolar cycloaddition is a versatile synthetic strategy to construct five-membered heterocycles of various types.[2—4] Nitrile oxides are one of the most reactive 1,3-dipoles widely used in the synthesis of five-membered *N*,*O*-containing azoles.[5] Like other unstable intermediates, nitrile oxides are usually generated *in situ* and further involved in cycloadditions with various dipolarophiles. Nitrile oxides are mainly generated by dehydrochlorination of hydroximoyl chlorides, thermal decomposition of nitrolic acids, and dehydration of nitroalkanes.[5,6]

Useful source of nitrile oxides is symmetrical furoxans, which can be regarded as dimers of nitrile oxides even if they were synthesized by other methods, for instance, by oxidation of the corresponding glyoximes.

Thermolysis of symmetrically substituted furoxans proceeds with cycloreversion to give two molecules of nitrile oxide. Cycloreversion of furoxans bearing aromatic and aliphatic substituents occurs at high temperatures and can be accompanied by isomerization of nitrile oxides into isocyanates. To exclude the possibility of isomerization, furoxans bearing bulky substituents, *e.g.*, adamantyl fragment,[7] or furoxans fused with strained carbocycles[8,9] are mainly used.

Cycloreversion of furoxans bearing electron-withdrawing substituents proceeds at lower temperature (80—110 °C) but accompanies by intramolecular migration of one of the functional groups at the furoxan cycle.[10,11]

We earlier have demonstrated[12] that dinitrofuroxan (DNFO) in the CCl_4 solution at 20 °C exists in equilibrium with its monomeric form, nitroformonitrile oxide (NFNO). We have succeeded to perform [3+2] cycloaddition of NFNO to cyano group of trichloroacetonitrile and methyl cyanoformate to give two 3-nitro-1,2,4-oxadiazole derivatives in low yields. However, our attempts to involve other dipolarophiles (phenylacetylene, *trans*-stilbene, and cyclohexene) in similar reactions led to unseparable product mixtures. Meanwhile, the synthesis of *N*,*O*-containing azole derivatives is still a challenge for organic chemists. For instance, it is well known[4] that isoxazoles and their partially hydrogenated analogs, isoxazolines, are promising building blocks in organic synthesis. These compounds possess a wide range of biological activities (antimicrobial, antiviral, antifungal[13]), can act as the ligands for a variety of glutamate receptors and γ-aminobutyric acid (GABA) receptors.[14,15] 3-Nitroisoxazoles are of interest as antimicrobial agents.[16]

[3+2] Cycloaddition of NFNO with acetylenes and olefins could be regarded as the simplest approach to 3-nitroisoxazoles and 3-nitroisoxazolines. However, the known methods for *in situ* generation of NFNO require aggressive media (treatment of dinitromethane potassium salt with either 30% oleum at 20 °C or 95% H_2SO_4 at 100 °C; nitration of 2-methyl-1-nitro-1-prop-1-ene with a mixture of concentrated sulfuric and nitric acids)[17,18] and cannot be applied in the reactions with dipolarophiles. The goal of the present work is the development of the tandem process involving *in situ* generation of NFNO *via* the DNFO cycloreversion with subsequent [3+2] cycloaddition between thus formed NFNO and different dipolarophiles.

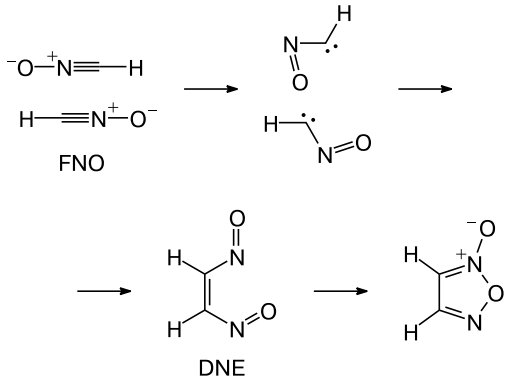
Taking into account the low effectiveness of our previous studies, we started present investigations from quantum chemical calculations of the possibility of generating NFNO by thermolysis of DNFO at 20 °C in organic sol-

* For short communication see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 0415—0422, February, 2015.

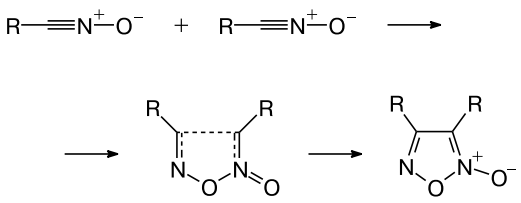
vent. For the reversible process "dimerization of formonitrile oxide—cycloreversion of unsubstituted furoxan", two mechanisms ("carbene" and concerted) have been suggested. Turs and co-workers[19] calculated potential energy surface for cyclodimerization of formonitrile oxide (FNO) by the MNDO and MINDO/3 semiempirical methods. The authors suggested that the cyclodimerization is a two stage process involving formation of intermediate *cis*-dinitrosoethylene (DNE) followed by the ring closure of the intermediate to give furoxan. In the transition state leading to DNE, two molecules of nitrile oxide are arranged perpendicular to each other forming the system similar to the carbenoid species (Scheme 1).

Scheme 1



Detailed kinetic study of nitrile oxide dimerization into furoxans[20,21] suggests the bimolecular concerted mechanism of nitrile oxide cyclodimerization of the 1,3-dipolar cycloaddition type (Scheme 2). However, this mechanism contradicts the Huisgen rule, which states that the direction of cycloaddition producing the highest energy gain upon formation of novel σ-bonds is favorable.[22]

Scheme 2



Taking into account the published data, we calculated cycloreversion of DNFO into two molecules of NFNO (both cycloreversion of DNFO into NFNO and cyclodimerization of NFNO into DNFO were regarded as reversible processes). Calculations were performed in gas phase and solvent phase (B3LYP/6-31G(d), point estimation with PCM for CCl_4 as a solvent). The reaction mechanisms were evaluated using Gibbs activation energy considering both enthalpic and entropic contributions. Calculations show that the activation energy of the transition state for the concerted mechanism is very high being 107.7 kcal mol^{-1} in gas phase (108.44 kcal mol^{-1} in solvent phase) and calculated Gibbs activation energy is 100.52 kcal mol^{-1}. Obviously, the concerted mechanism of the studied process is unlikely and, therefore, cycloreversion of DNFO into NFNO was calculated *via* "carbene" mechanism[19] using not only the B3LYP/6-31G(d) method but also the M05-2X/6-31G(d) level of theory.

Energy diagrams of cycloreversion of DNFO to give two molecules of NFNO were plotted using Gibbs activation energy calculations in gas phase at 298 K as most correctly describing the reaction mechanism (Fig. 1). According to the B3LYP/6-31G(d) calculations, the barriers of the transformation of DNFO into DNE are 35.04 kcal mol^{-1} in gas phase (the change in the Gibbs free energy is −6.00 kcal mol^{-1}) and 35.17 kcal mol^{-1} in the CCl_4 solution (the Gibbs activation energy is 31.8 kcal mol^{-1}). The activation energies for the second stage, transformation of DNE into two molecules of NFNO, are 19.72 kcal mol^{-1} in gas phase (the change in the Gibbs free energy is −6.45 kcal mol^{-1}) and 19.64 kcal mol^{-1} in solvent phase (the Gibbs activation energy is 17.87 kcal mol^{-1}). The calculations reveal that the solvent does not virtually affect the activation energy of the reaction. Therefore, further M05-2X/6-31G(d) calculations were carried out only for gas phase (see Fig. 1).

Calculations performed by both methods indicate that cycloreversion of DNFO is a two-stage process. The first stage involves the cleavage of the O(1)—N(2) bond, the weakest bond of the furoxan cycle (transition state **TS-1**) to give DNE. On the second stage proceeding *via* transition state **TS-2**, the C(3)—C(4) bond of DNE is cleaved. Some differences in calculated values have to be noted. According to the B3LYP/6-31G(d) calculations, the first stage is thermodynamically favorable; in contrast, the M05-2X/6-31G(d) calculations show that the second stage is more favorable. However, the total energies of the processes calculated by both methods are rather similar.

Calculations indicate that the reverse process (cyclodimerization of NFNO into DNFO) is energetically more favorable. However, the experimental data[12] demonstrate the possibility of cycloreversion, at least for activated nitriles. Apparently, the driving force of this process is a considerable energy gain obtained upon formation of 1,2,4-oxadiazole derivatives. Therefore, before the experimental studies of other dipolarophiles, we calculated activation barriers and reaction energies for [3+2] cycloaddition between NFNO and three different electron-deficient dipolarophiles, namely, methyl propiolate (**1a**), methyl acrylate (**2a**), and trichloroacetonitrile (**3**). Energy diagrams for the addition of NFNO to these dipolarophiles are given in Figs 2—4. Calculations were carried out on the B3LYP/6-31G(d) level of theory for both the Michael

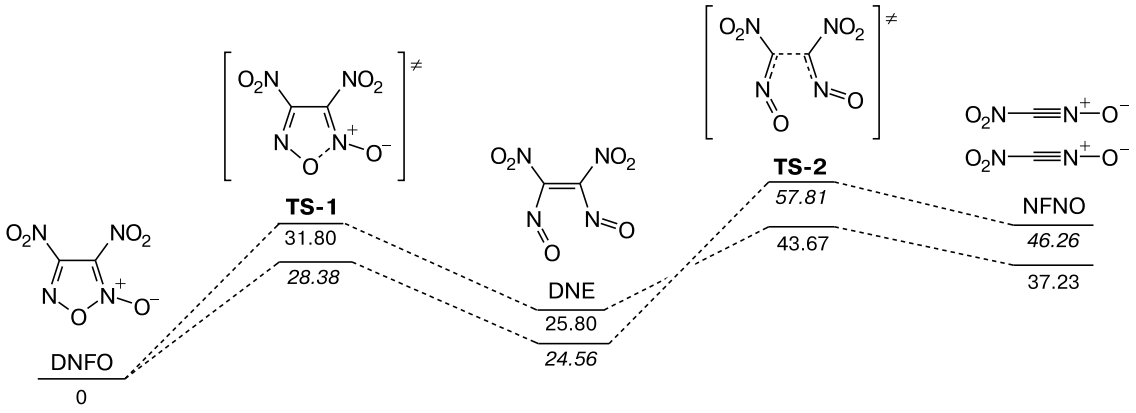


Fig. 1. Energy diagram for the DNFO—NFNO cycloreversion. Activation Gibbs energies (kcal mol^{-1}) calculated in gas phase by B3LYP/6-31G(d) and M05-2X/6-31G(d) are given in roman type and italic, respectively.

(pathway ***a***, **TS-M**) and anti-Michael (pathway ***b***, **TS-AM**) additions. Calculations indicate that for all three dipolarophiles, anti-Michael cycloaddition is an energetically favorable and produces 5-methoxycarbonyl-3-nitroisoxazole (**4a**), 5-methoxycarbonyl-3-nitroisoxazoline (**5a**), and 3-nitro-5-trichloromethyl-1,2,4-oxadiazole (**6**), respectively.

According to the energy diagrams (see Figs 2—4), cycloaddition of NFNO with dipolarophiles of all three types is a one-stage process and proceeds without formation of any intermediates. It also should be mentioned that formation of nitroazoles **4a**, **5a**, **6** gains significant energy. Meanwhile, a comparison of diagrams 2—4 shows noticeable differences between trichloroacetonitrile and two other dipolarophiles upon formation of Michael-type cycloadducts. To explain this difference, we calculated the NPA[23] charge distribution on the reacting atoms of dipolarophiles and NFNO. Calculated charges on the N and C atoms in trichloroacetonitrile (**3**) are –0.217 and +0.213 a.u., respectively. For methyl propiolate (**1a**) and methyl acrylate (**2a**), the charges on the reacting atoms are similar being –0.13 and –0.14 a.u. for methyl propiolate and –0.33 and –0.34 for methyl acrylate. For NFNO, the charges on the C and O atoms are +0.25 and –0.27 a.u., respectively. These data indicate that trichloroacetonitrile (**3**) cannot react with NFNO following the Michael type mechanism.

It should be emphasized that in contrast to cycloreversion of DNFO, [3+2] cycloadditions shown on Figs 2—4 are irreversible and no data on the possibility of cycloreversion for azoles of type **4**—**6** have been published.[3,4] Therefore, the performed calculations allowed us to expect that generation of NFNO *via* cycloreversion of DNFO with subsequent cycloaddition with different dipolarophiles can be successful.

We started experimental studies from [3+2] cycloaddition of NFNO in commonly used CCl_4 using following substituted terminal and internal acetylenes and ethylenes as dipolarophiles: methyl propiolate (**1a**), dimethyl acetylenedicarboxylate (**1b**), but-2-yne-1,4-diol (**1c**), methyl acrylate (**2a**), dimethyl fumarate (**2b**), and dimethyl maleate (**2c**). Since the concentration of NFNO in the reaction mixture is very low, dipolarophiles were used in 5-fold excess with respect to DNFO. Dipolarophiles **1a**—**c** and **2a**—**c** are found to be reactive in cycloaddition leading to 3-nitroisoxazoles **4a**—**c** and 3-nitroisoxazolines **5a**—**c**

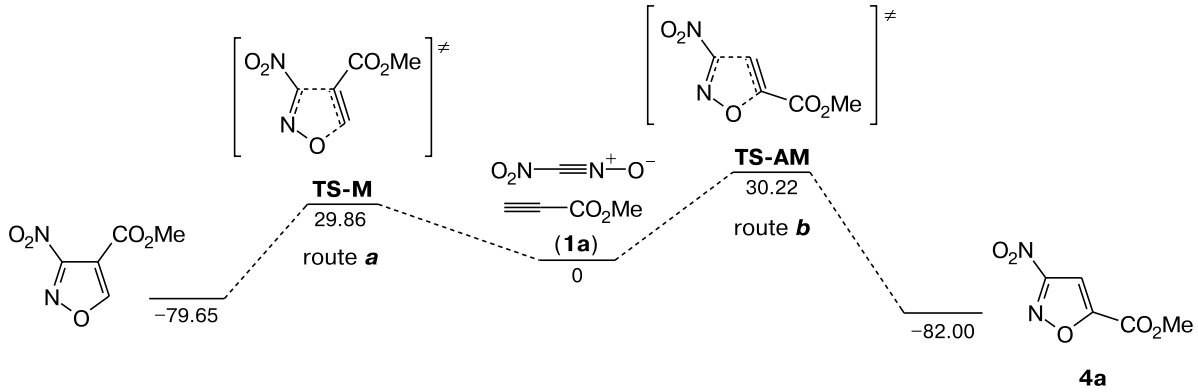


Fig. 2. Energy diagram (free Gibbs energies (kcal mol^{-1})) for [3+2] cycloaddition of methyl propiolate (**1a**) to NFNO.

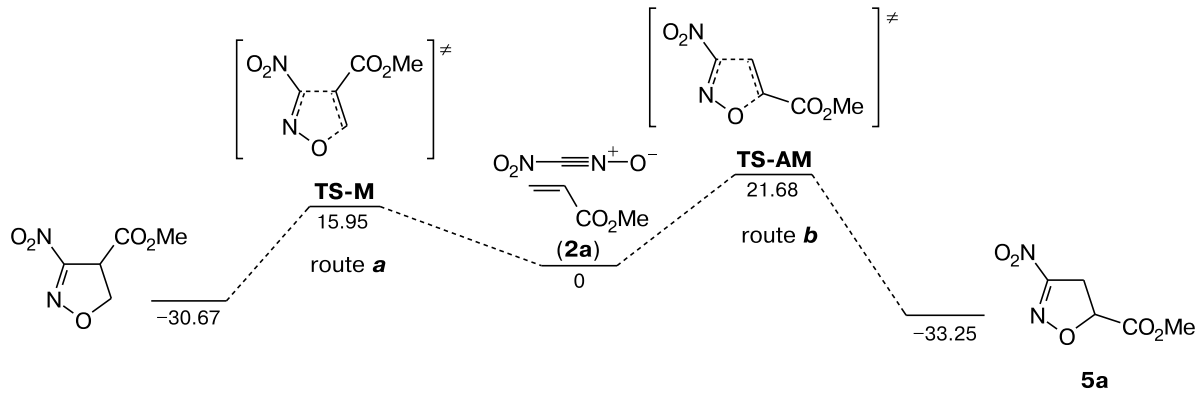


Fig. 3. Energy diagram (free Gibbs energies (kcal mol^{-1})) for [3+2] cycloaddition of methyl acrylate (**2a**) to NFNO.

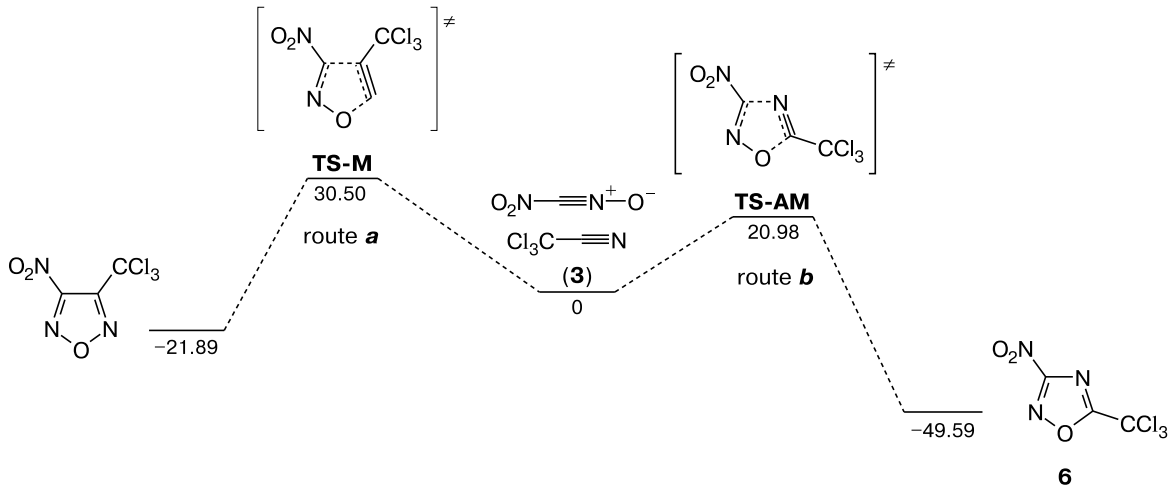


Fig. 4. Energy diagram (free Gibbs energies (kcal mol^{-1})) for [3+2] cycloaddition of trichloroacetonitrile (**3**) to NFNO.

(Scheme 3, Table 1). However, in all cases, the reaction times were relatively long (from 36 h to 10 days, TLC monitoring of the DNFO consumption) and the product yields were low (see Table 1). Apparently, under applied conditions, significant amount of DNFO decomposes rather than underwent cycloreversion. From other tested dipolarophiles, only hexafluoroacetone (**7**) is found to be reactive to give 3-nitro-1,4,2-dioxazole **8a**. Phenyl vinyl sulfone and diphenyl cyclopropenone do not react under described conditions. Nevertheless, the obtained experimental data confirm both the correctness of modeled mechanism of the DNFO decomposition into two NFNO species and possibility of the generated NFNO to undergo [3+2] cycloaddition.

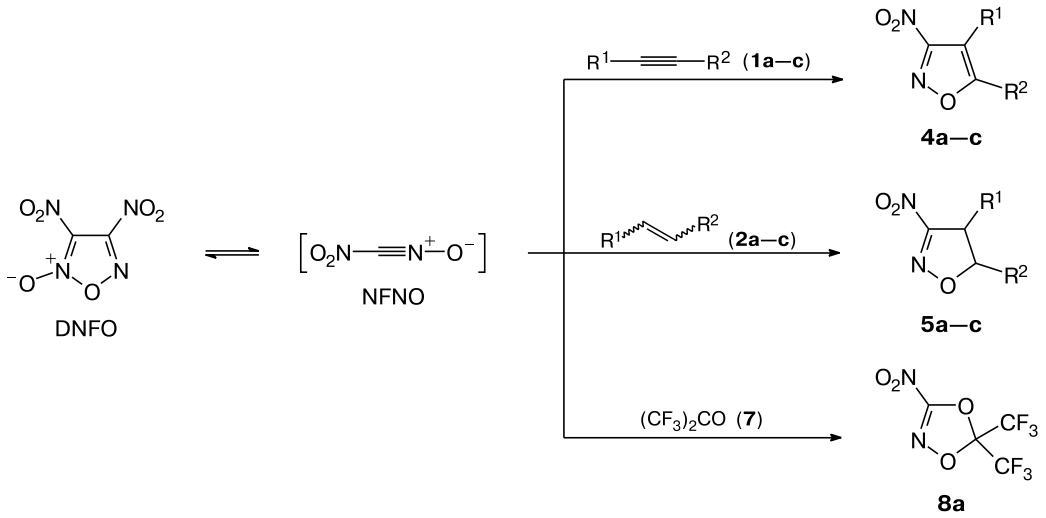
In recent years, ionic liquids (ILs) are widely used as the reaction media and catalysts for various heterolytic processes. Ionic liquids comprising non-coordinated ionic pairs are the ideal ionic surrounding for polar intermediates. Application of ILs leads to noticeable increase in the rate and selectivity of the reaction.[24–26] Ionic liquids possess unique physicochemical properties being non-flammable and non-volatile. Therefore, ILs favor transformations that cannot be achieved in common organic solvents.[27,28] Our research group has a positive experience in carrying out chemical reactions including 1,3-dipolar

Table 1. [3+2] Cycloaddition of NFNO to dipolarophiles in CCl_4 (method ***A***)

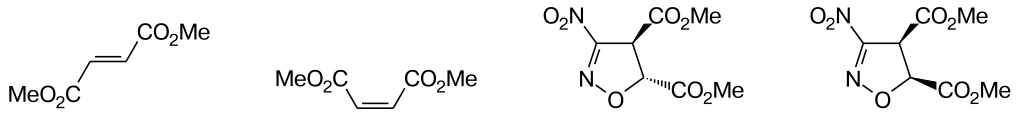
Dipolarophile	Product[a]	*t*/h	Yield[b] (%)
1a	**4a**	48	19
1b	**4b**	48	31
1c	**4c**	72	22
2a	**5a**	120	50
2b	**5b**	168	30
2c	**5c**	240	10
7	**8a**	120	14

[a] Structures of all products were established by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy, mass spectrometry, and microanalysis.
[b] Isolated yield.

Scheme 3



R^1 = H, R^2 = COOMe (**1a**, **2a**, **4a**, **5a**);
R^1 = R^2 = COOMe (**1b**, **2b**, **2c**, **4b**, **5b**, **5c**), CH_2OH (**1c**, **4c**)



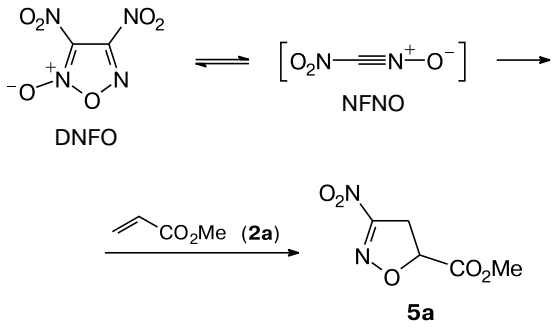
cycloaddition[29—31] in ILs; therefore, we decided to apply ILs for promoting cycloaddition between NFNO and different dipolarophiles.

With this aim, we optimized the reaction conditions by the example of the cycloaddition of DNFO and methyl acrylate (Scheme 4). As IL, we first used readily available IL, [bmim]BF_4 (bmim is 1-butyl-3-methylimidazolium). An attempt to use [bmim]BF_4 as the reaction medium resulted in DNFO explosive decomposition; therefore, all further reactions were carried out utilizing catalytic amounts of [bmim]BF_4 and CCl_4 as a solvent. Optimum amount of IL was found to be 40 mol.%. The similar results were obtained in the presence of catalytic amounts of other ILs ([emim]OTf, [emim]HSO_4, emim is 3-ethyl-1-methylimidazolium). Note that the reaction time and the yield of 3-nitroisoxazoline **2a** do not depend on the nature of IL and all further experiments were carried out with 40 mol.% [bmim]BF_4.

Before starting the studies on the cycloaddition of NFNO with other dipolarophiles, we performed a screening of the molar excess of dipolarophile with respect to DNFO by the example of methyl acrylate carring out the reaction under above described conditions. A ratio of dipolarophile : DNFO = 5 : 1 was found to be the optimum.

As expected, the rates of IL-catalyzed 1,3-dipolar cycloaddition of already studied dipolarophiles **1a—c**, **2a—c**, and **7** with NFNO were noticeably higher (Table 2). Moreover, we succeeded to perform cycloadditions with dipolarophiles (Fig, 5), which were found inactive in the reactions with NFNO in CCl_4 in this work (compounds **2e**,**f**) and in our previous study (compounds **1d**, **2d**).[12] The corresponding nitroazoles **4d** and **5d—f** were obtained in moderate yields. The reaction rate for cycloaddition involving trichloroacetonitrile (**3**) was also higher. Among other carbonyl compounds, 3-acetyl-4-aminofuroxan (**9**) was reactive in cycloaddition to give nitroazole **8b**.

Scheme 4



In summary, we developed a novel general approach towards nitroazoles *via* [3+2] cycloaddition of different

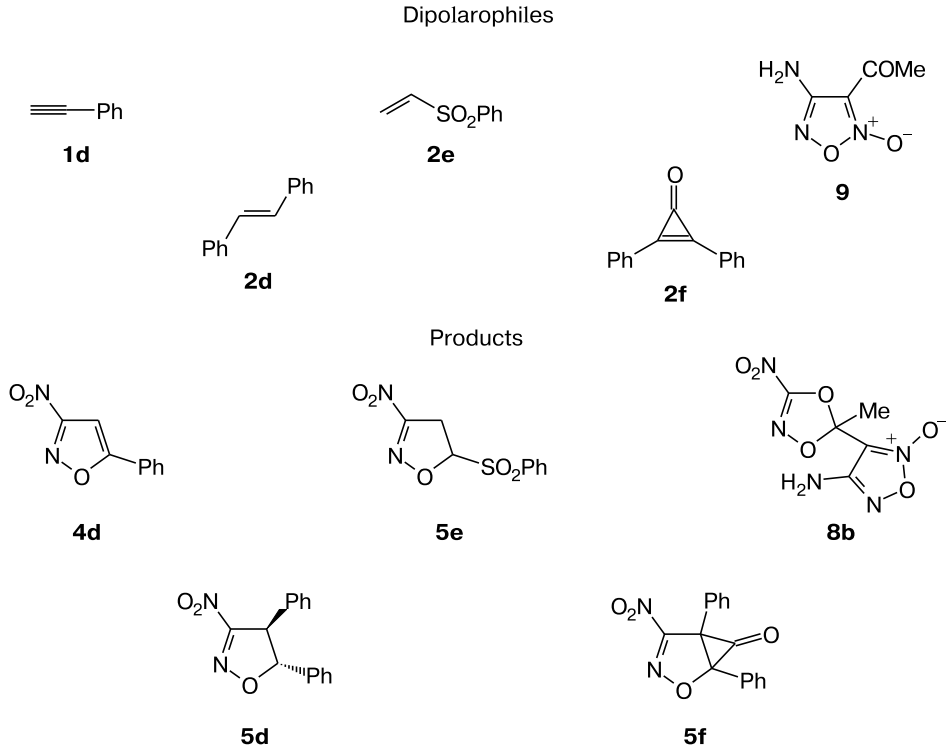


Fig. 5. Structures of dipolarophiles **1d**, **2d**—**f**, **9** and products of their [3+2] cycloaddition to NFNO.

dipolarophiles with NFNO generated *in situ* by cycloreversion of DNFO. It was found that catalysis with ILs significantly accelerates the cycloaddition and allows involving in the reaction dipolarophiles inactive in organic solvents. Preliminary quantum chemical calculations suggest mechanism of the DNFO cycloreversion and show the possibility to perform cycloaddition of NFNO generated by the DNFO cycloreversion with dipolarophiles.

Table 2. IL-Catalyzed [3+2] cycloaddition of NFNO to dipolarophiles[a] (method ***B***)

Dipolarophile	Product[b]	*t*/h	Yield[c] (%)
1a	**4a**	12	22
1b	**4b**	12	24
1c	**4c**	12	21
1d	**4d**	12	26
2a	**5a**	36	32
2b	**5b**	48	38
2c	**5c**	72	32
2d	**5d**	72	26
2e	**5e**	72	14
2f	**5f**	36	23
7	**8a**	48	19
9	**8b**	48	24
3	**6**	48	23

[a] Structures of dipolarophiles **1d**, **2d**—**f**, **9** and products of their [3+2] cycloaddition to NFNO, compounds **4d**, **5d**—**f**, **8b**, are given in Fig. 5.

[b] Structures of all products were established by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy, mass spectrometry, and microanalysis.

[c] Isolated yield.

Experimental

^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded with a Bruker AM-300 instrument (working frequencies of 300, 75, and 21 MHz, respectively) in $CDCl_3$. The chemical shifts are given in the δ scale relative to the residual proton signal of $CDCl_3$ (δ_H 7.27) and signal of the C atom (δ_C 77.0). High resolution electrospray ionization mass spectra were obtained on a Bruker micrOTOF II instrument. Melting points were determined with a Sanyo Gallenkamp apparatus. The course of the reactions were monitored by TLC on precoated Merck 60 F_{254} plates. Products were purified by column chromatography on silica gel 60 A (0.060—0.200 mm, Acros Organics); elution with CH_2Cl_2—CCl_4 or $CHCl_3$.

Physicochemical data for compounds **4a**—**d**, **5a**—**f**, **6**, and **8a** are given in Ref. 1 (see Supporting Information Section). Compound **8b** was first synthesized in the present work. Dinitrofuroxan was synthesized following the known procedure.[18]

Synthesis of compounds 4a—c, 5a—c, and 8a (general procedure). Method *A*. To a stirred solution of dinitrofuroxan (100 mg, 0.57 mmol) in CCl_4 (2 mL), the corresponding dipolarophile (2.85 mmol) was added at room temperature. The reac-

tion mixture was stirred until complete consumption of the starting dinitrofuroxan (TLC monitoring), then water (5 mL) was added, the organic layer was separated, and the aqueous layer was extracted with CCl_4 (3×3 mL). The combined organics were washed with water and dried with $MgSO_4$. Removal of the solvent *in vacuo* and purification of the residue by silica gel column chromatography afforded target product.

Synthesis of compounds 4a—d, 5a—f, 6, and 8a,b (general procedure). Method *B*. To a stirred solution of dinitrofuroxan (100 mg, 0.57 mmol) in CCl_4 (2 mL), $[bmim]BF_4$ (51 mg, 0.228 mmol) and the corresponding dipolarophile (2.85 mmol) were added at room temperature. The reaction was carried out and the products were isolated following the method *A*.

Caution! Dinitrofuroxan has to be used only in solution in CCl_4 due to its tendency to explode.

4-Amino-3-(5-methyl-3-nitro-1,4,2-dioxazol-5-yl)furoxan (8b). Yield 31 mg (24%, method *B*). Yellow powder, m.p. 88—89 °C. R_f 0.43 ($CHCl_3$). ^{1}H NMR, δ: 2.93 (s, 3 H, CH_3); 5.24 (br.s, 2 H, NH_2). ^{13}C NMR, δ: 14.2 (CH_3); 110.2 (C(3) furoxan cycle); 139.4 (C(5) dioxazole cycle); 150.2 (C—NH_2); 164.8 (C—NO_2). ^{14}N NMR, δ: –40.3 (br.s, NO_2). Found, *m/z*: 232.0665 $[M + H]^+$. $C_5H_5N_5O_6$. Calculated, *m/z*: 232.0273.

Quantum chemical calculations were carried out in the density functional theory (DFT) framework using Gaussian 98 software.[32] The structures corresponding to the global minimum and reaction products were localized by DFT using the B3LYP hybrid exchange correlation functional with the 6-31G(d) split valence basis set by M05-2X method. Stationary points were located by the Hessian matrix calculations by the absence of the imaginary frequencies.

Authors are grateful to Merck KGaA for kindly providing ionic liquids.

This work was financially supported in parts by the Russian Academy of Sciences (Program "Development of Methods for the Synthesis of Chemical Compounds and Design of Novel Materials").

References

1. L. L. Fershtat, I. V. Ovchinnikov, N. N. Makhova, *Tetrahedron Lett.*, 2014, **55**, 2398.
2. R. Huisgen, *Angew. Chem., Int. Ed.*, 1963, **2**, 565.
3. A. Padwa, W. H. Pearson, in *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products*, Ed. H. Feuer, Wiley-VCH, New York, 2002, p. 363.
4. P. Grünanger, P. Vita-Finzi, *Isoxazoles, Part I*, in *The Chemistry of Heterocyclic Compounds*, Eds E. C. Taylor, A. Weissberger, Wiley, New York, 1991, Vol. **49**, p. 1.
5. C. Grundmann, P. Grünanger, *The Nitrile Oxides*, Springer-Verlag, Berlin—Heidelberg—New York, 1971.
6. L. I. Khmel´nitskii, S. S. Novikov, T. I. Godovikova, *Khimiya furoksanov. Stroenie i sintez* [*Chemistry of Furoxans: Structure and Synthesis*], Nauka, Moscow, 1996, 383 pp. (in Russian).
7. A. Dondoni, G. Barbaro, A. Battaglia, P. Giorgianni, *J. Org. Chem.*, 1972, **37**, 3196.
8. J. F. Barnes, M. J. Barrow, M. M. Harding, R. M. Paton, P. L. Ashcroft, J. Crosby, C. J. Joyce, *J. Chem. Res.* (*M*), 1979, 3601.
9. A. S. Kulikov, M. A. Epishina, I. V. Ovchinnikov, N. N. Makhova, *Russ. Chem. Bull.* (*Int. Ed.*), 2007, **56**, 1580 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1521].
10. I. V. Seregin, I. V. Ovchinnikov, N. N. Makhova, D. V. Lyubetsky, K. A. Lyssenko, *Mendeleev Commun.*, 2003, **13**, 230.
11. D. R. Brittelli, G. A. Boswell, *J. Org. Chem.*, 1981, **46**, 316.
12. I. V. Ovchinnikov, N. A. Popov, N. N. Makhova, L. I. Khmel´nitskii, V. A. Shlyapochnikov, *Mendeleev Commun.*, 1995, **5**, 231.
13. D. Giomi, F. M. Cordero, F. Machetti, in *Comprehensive Heterocyclic Chemistry III*, Eds A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor, Elsevier, Oxford, 2008, Vol. **4**, p. 365.
14. M. Pieroni, A. Lilienkampf, B. Wan, Y. Wang, S. G. Franzblau, A. P. Kozikowski *J. Med. Chem.*, 2009, **52**, 6287.
15. D. Simoni, R. Rondanin, R. Baruchello, M. Rizzi, G. Grisolia, M. Eleopra, S. Grimaudo, A. Di Cristina, M. R. Pipitone, M. R. Bongiorno, M. Arico, F. P. Invidiata, M. Tolomeo, *J. Med. Chem.*, 2008, **51**, 4796.
16. US Pat. Appl. 6638958; *Chem. Abstr.*, 2003, **166**, 698.
17. I. V. Ovchinnikov, N. N. Makhova, L. I. Khmel´nitskii, *Mendeleev Commun.*, 1993, **3**, 210.
18. I. V. Ovchinnikov, N. N. Makhova, L. I. Khmel´nitskii, *Russ. Chem. Bull.* (*Engl. Transl.*), 1995, **44**, 702 [*Izv. Akad. Nauk*, *Ser. Khim.*, 1995, 722].
19. V. É. Turs, N. M. Lyapin, V. A. Shlyapochnikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1982, **31**, 202 [*Izv. Akad. Nauk*, *Ser. Khim.*, 1982, 214].
20. G. Barbaro, A. Battaglia, A. Dondoni, *J. Chem. Soc. B*, 1970, 588.
21. A. Dondoni, A. Mangini, S. Ghersetti, *Tetrahedron Lett.*, 1966, **39**, 4789.
22. R. Huisgen, *Angew. Chem.*, 1963, **78**, 604.
23. A. E. Reed, F. J. Weinhold, *Chem. Phys.*, 1983, **78**, 4066.
24. *Ionic Liquids in Synthesis*, Vol. **1**, Eds P. Wasserscheid, T. Welton, Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, Germany, 2008, 367 pp.
25. *Ionic Liquids in Synthesis*, Vol. **2**, Eds P. Wasserscheid, T. Welton, Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, Germany, 2008, 353 pp.
26. I. R. Siddiqui, S. S. Shamim, M. A. Waseem, A. A. H. Abumhdi, A. Srivastava, A. Srivastava, *Tetrahedron Lett.*, 2013, **54**, 5083.
27. Yu. S. Syroeshkina, V. V. Kuznetsov, V. V. Kachala, N. N. Makhova, *J. Heterocycl. Chem.*, 2009, **46**, 1195.
28. V. Yu. Petukhova, L. L. Fershtat, V. V. Kachala, V. V. Kuznetsov, D. V. Khakimov, T. S. Pivina, N. N. Makhova, *J. Heterocycl. Chem.*, 2013, **50**, 326.
29. S. G. Zlotin, N. N. Makhova, *Russ. Chem. Rev.*, 2010, **79**, 543.
30. S. G. Zlotin, N. N. Makhova, *Mendeleev Commun.*, 2010, **20**, 63.
31. N. N. Makhova, M. I. Pleshchev, M. A. Epishina, A. S. Kulikov, *Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2014, **50**, 634 [*Khim. Geterotsikl. Soedin.*, 2014, 690].
32. M. J. Frish, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Mont-

gomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, G. Liu, A. Liashenko, P. Piskorz, I. Komazomi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzales, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN 98*, *Revision A.9*, Gaussian, Inc., Pittsburgh (PA), 1998.

Received September 22, 2014;
in revised form October 20, 2014