Available online at www.sciencedirect.com

ScienceDirect

Focus Article, *Mendeleev Commun.*, 2022, **32**, 703–713

Mendeleev Communications

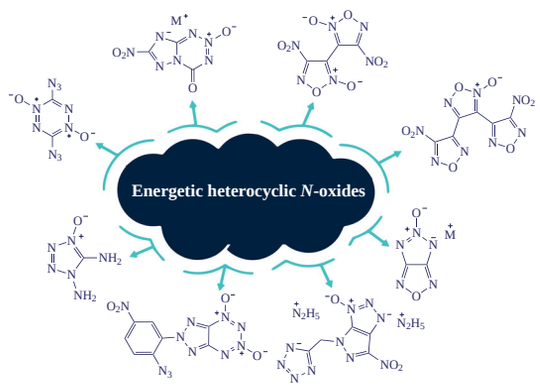
Energetic heterocyclic *N*-oxides: synthesis and performance

Alexander A. Larin and Leonid L. Fershtat*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: fershtat@bk.ru

DOI: 10.1016/j.mencom.2022.11.001

Novel synthetic strategies toward construction and functionalization of nitrogen-rich energetic compounds bearing at least one heterocyclic *N*-oxide scaffold are briefly overviewed. The present focus review summarizes main recent advances (published in the period 2017–2022) in the chemistry of five- and six-membered heterocyclic *N*-oxides as well as their linear combinations and fused bi-, tri- and tetraheterocyclic frameworks which are of paramount importance for the development of next-generation energetic materials. Physicochemical properties along with detonation performance and mechanical sensitivities of the reported high-energy substances are discussed and their application potential is especially emphasized.

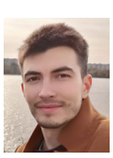


Keywords: energetic materials, nitrogen heterocycles, fused heterocycles, detonation performance, *N*-oxides, synthetic methodologies.

1. Introduction

Functional organic materials are one of the most important and emerging areas of research in state-of-the-art materials science. Construction of potential high-performance materials as well as their essential components is needed to be achieved according to modern requirements of sustainable and environmentally-focused society. This issue is still relevant in the field of energetic materials science.[1–3] Performance and sensitivity of currently used high-energy compounds (TNT: 2,4,6-trinitrotoluene, NTO: 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one, RDX: 1,3,5-trinitro-1,3,5-triazinane, HMX: 1,3,5,7-tetranitro-1,3,5,7-tetrazocine, PETN: pentaerythritol tetranitrate, CL-20: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) are usually unbalanced, while their ecological and toxicological profiles are unfavorable. In this regard, preparation of novel eco-friendly energetic materials with high nitrogen content and acceptable safety requirements remains urgent.[4,5]

A search for novel energetic materials continues to evolve and nowadays it is performed among a variety of high-nitrogen and nitrogen-oxygen heterocyclic compounds.[6–9] A utilization of hetarene scaffolds for the construction of high-energy structures has a number of advantages compared to the cyclic and caged nitramines. Polynitrogen and nitrogen-oxygen heterocyclic derivatives have higher densities due to planarity and possess higher enthalpies of formation, thus providing high detonation performance of such materials. In this regard, incorporation of the *N*-oxide functionality into the heterocyclic core additionally improves the crystal packing of the molecule resulting in an increased density and decreased sensitivity to mechanical stimuli of the target energetic materials.[10] Moreover, the presence of the *N*-oxide functionality enables tunability of the corresponding heterocyclic derivatives regarding their potential relevance to various energetic formulations. Therefore, this review covers recent synthetic strategies toward construction and functionalization of nitrogen-rich energetic compounds bearing at least one heterocyclic *N*-oxide scaffold. Five- and six-membered heterocyclic *N*-oxides as well as their linear combinations and fused bi-, tri- and tetraheterocyclic frameworks were summarized and their physicochemical and detonation properties were reviewed.

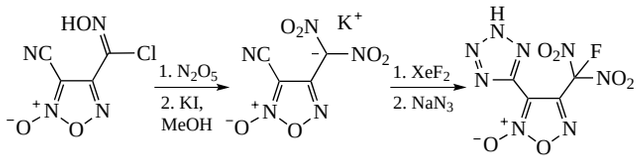


Dr. Alexander A. Larin is a researcher of the Laboratory of Nitrogen Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. His scientific interests include development of novel synthetic methodologies in the field of nitrogen heterocycles, especially, high-energy 1,2,5-oxadiazoles 2-oxides (furoxans). He has about 20 research papers and reviews in peer-reviewed journals.

Dr. Leonid L. Fershtat is the head of Laboratory of Nitrogen Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. His scientific interests include creation of novel synthetic strategies in the field of nitrogen heterocycles, and search for pharmacologically active and high energy heterocyclic derivatives. He has about 80 research papers and reviews in peer-reviewed journals.

2. Monocyclic five-membered heterocyclic *N*-oxides and their linear combinations

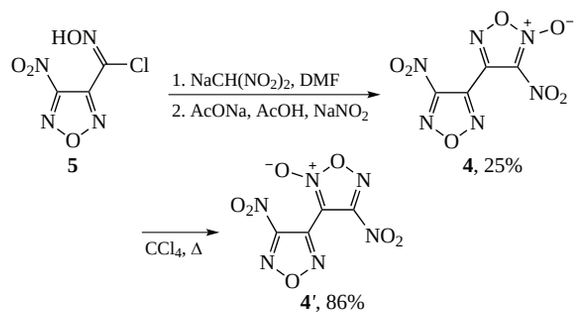
In a series of energetic five-membered heterocyclic *N*-oxides the main efforts of researchers were directed towards a selective functionalization of the furoxan (1,2,5-oxadiazole 2-oxide) ring.[11–15] Such substrate specificity is attributed to the substantial explosophoric nature of the furoxan ring itself as well as to the presence of an additional oxygen atom in a combination with the *N*-oxide one. For example, nitration of the readily available chloroxime **1** followed by reduction of the *in situ* formed chlorodinitromethyl derivative resulted in a formation of potassium salt **2**. Compound **2** was further fluorinated, while the nitrile moiety was converted to the tetrazole ring (Scheme 1). Such combination of the furoxan ring with additional explosophores endowed compound **3** high enthalpy of formation (326.4 kJ mol^{-1}) and high experimental density (1.89 g cm^{-3}). In addition, furoxan **3** showed superior calculated detonation performance (D = 8.9 km s^{-1}, P = 36 GPa), which was comparable to that of RDX.[16]



1 **2**, 72% **3**, 67%

Scheme 1

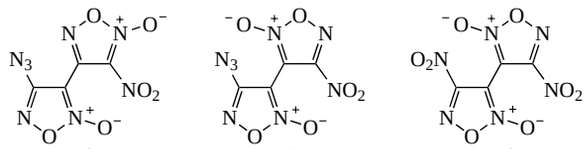
A number of approaches was created to synthesize linear biheterocyclic assemblies incorporating at least one furoxan ring. In particular, two hydrogen-free regioisomeric (nitrofurazanyl)nitrofuroxans **4** and **4′** were prepared *via* cascade reactions of chloroxime **5**. The 3-nitrofuroxan motif in compound **4** was isomerized to the corresponding 4-nitrofuroxan subunit *via* refluxing in CCl_4 (Scheme 2). Both compounds **4** and **4′** possess excellent detonation performance (D = 9.18–9.23 km s^{-1}, P = 38.8–39.4 GPa) comparable to that of HMX (D = 9.14 km s^{-1}, P = 39.2 GPa), while the thermal stability of isomer **4** is somewhat higher than that of **4′**.[17]



5 **4**, 25% **4′**, 86%

Scheme 2

Later, analogous approach was used for the preparation of 4-amino-3′-nitro-3,4′-bifuroxan[18] and regioisomeric bifuroxans **6**–**8** bearing azido and nitro functionalities (Figure 1).[19] 4-Azido-3′-nitro-3,4′-bifuroxan **6** has good oxygen balance (+6.25% to CO) and detonation performance (D = 8.95 km s^{-1}, P = 35.2 GPa) superior to nitroglycerine (D = 7.80 km s^{-1}, P = 25.6 GPa) which along with its lower sensitivity to impact (IS for **6**: 0.7 J, IS for nitroglycerine: < 0.2 J) make this material a promising component of smokeless powder. Possessing the same oxygen balance, regioisomeric 4-azido-4′-nitro-3,3′-bifuroxan **7** has lower mechanical sensitivity (IS = 2 J, FS = 32 N), better detonation properties (D = 9.28 km s^{-1}, P = 38.9 GPa) and may be recommended as a promising replacement of PETN (D = 8.40 km s^{-1}, P = 31.9 GPa). Another

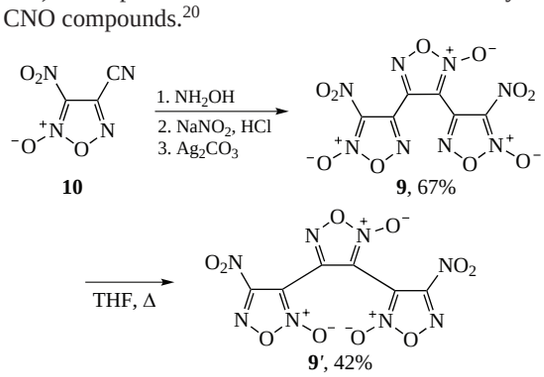


6 **7** **8**

Figure 1

representative bifuroxan, namely, 4,4′-dinitro-3,3-bifuroxan **8**, which was prepared upon oxidation of the corresponding diamine, has a zero oxygen balance to CO_2 and superior detonation performance (D = 9.75 km s^{-1}, P = 45.0 GPa), while its heat of explosion exceeds even benchmark explosive CL-20.[19]

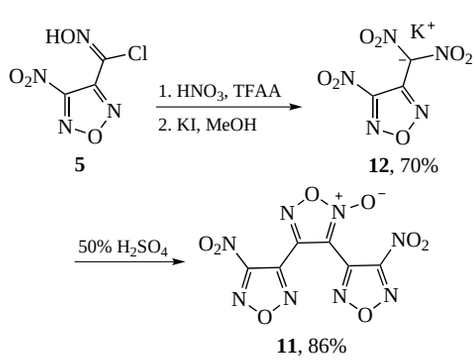
The synthetic pathway to regioisomeric trifuroxans **9** and **9′** is shown in Scheme 3. 3-Nitro-4-cyanofuroxan **10** was transformed to the corresponding chloroxime which was subjected to dehydrochlorination under the action of Ag_2CO_3 as a base to generate the corresponding nitrile oxide followed by its dimerization to form target energetic compound **9**. Isomerization of both 3-nitrofuroxan motifs occurred in refluxing THF and provided 4-nitrofuroxan **9′** in a yield of 42%. Advantageously, structure **9** has an extremely high crystal density (1.983 g cm^{-3} at 296 K) in comparison to other heteroaromatic-based hydrogen-free CNO compounds.[20]



10 **9**, 67% **9′**, 42%

Scheme 3

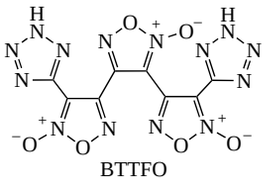
Unexpected formation of bis(nitrofurazanyl)furoxan **11** was observed upon acidification of the dinitromethylfuroxanate potassium salt **12**, which was in turn prepared through tandem nitration–reduction sequence of chloroxime **5** (Scheme 4). Compound **4** exhibited high densitiy (1.81 g cm^{-3}), excellent detonation properties and moderate sensitivities to impact and friction (IS = 14 J, FS = 360 N).[21]



5 **12**, 70% **11**, 86%

Scheme 4

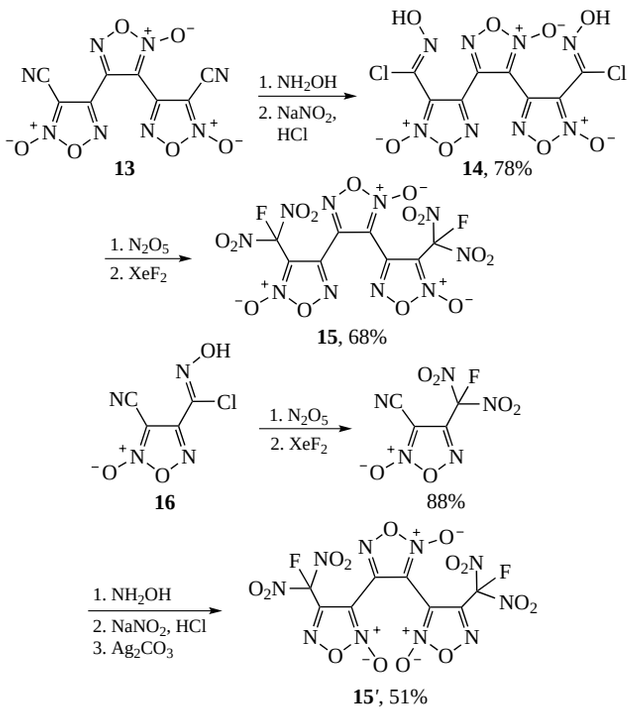
Terfuroxan (BTTFO) bearing two tetrazole rings (Figure 2) synthesized from the readily available dicyanofuroxan exhibited high enthalpy of formation (1291 kJ mol^{-1}), high decomposition temperature (202 °C) and good calculated detonation properties (D = 8.6 km s^{-1}, P = 31.5 GPa).[22]



BTTFO

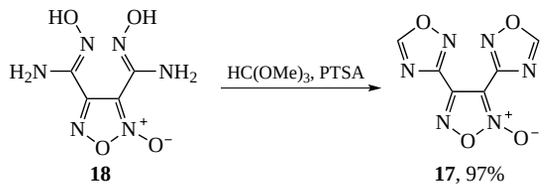
Figure 2

Even more energetic terfuroxan derivatives were obtained upon implementation of the fluorodinitromethyl group. Dicyanoterfuroxan **13** was converted to the corresponding bis(chloroxime) **14** which underwent nitration–reduction–fluorination protocol to afford bis(fluorodinitromethyl)-terfuroxan **15**. Isomer **15′** was obtained through the inverted reaction scheme starting from cyanofuroxan **16** (Scheme 5). Compound **15** has higher density (2.00 g cm^{-3}) than isomer **15′** (1.91 g cm^{-3}) and, as a result, superior detonation performance (D = 9.5 km s^{-1}, P = 42.6 GPa), which is comparable to CL-20 and exceeds that of isomer **15′** (D = 9.2 km s^{-1}, P = 38.8 GPa).[23]



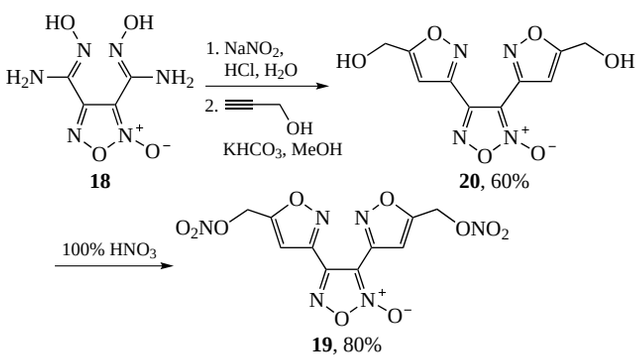
Scheme 5

Other dihetarylfuroxans are also considered as attractive candidates for various energetic applications. For example, bis(1,2,4-oxadiazolyl)furoxan **17** is a promising material for melt-cast compositions which is insensitive to mechanical stimuli and electrostatic discharge and exhibits calculated detonation pressure 20% higher than that of TNT.[24] Although initially compound **17** was obtained by our team through Sc(OTf)$_3$-catalyzed heterocyclization of bis(amidoxime) **18** with trimethyl orthoformate,[25] Sabatini group improved its preparation and scalability using PTSA as an acid catalyst, which enabled a preparation of compound **17** with almost quantitative yield (Scheme 6).[24]



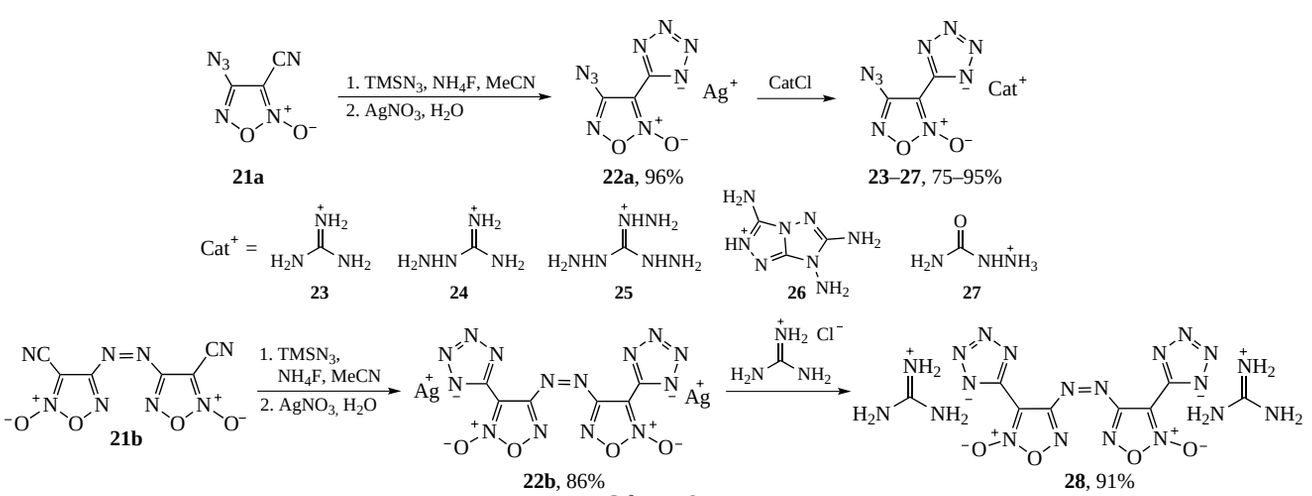
Scheme 6

Bis(amidoxime) **18** was used as a precursor to another furoxan-based melt-cast explosive – bis(nitroxymethyl-isoxazolyl)furoxan **19**. Synthesis of compound **19** was accomplished through an intermediate formation of the corresponding bis(chloroxime) followed by base-mediated generation of bis(nitrile oxide) which underwent [3+2] cycloaddition to propargyl alcohol to afford bis(hydroxymethyl) derivative **20**. Nitration of compound **20** resulted in a formation of the nitrate **19** in a good yield. Energetic material **19** features an insensitive behavior to impact, friction, and electrostatic discharge, with a calculated detonation pressure about 25% higher than the state-of-the-art melt-castable explosive TNT (Scheme 7).[26]



Scheme 7

Next-generation furoxan-based energetic materials were synthesized through an oxidative N–N coupling of (amino-

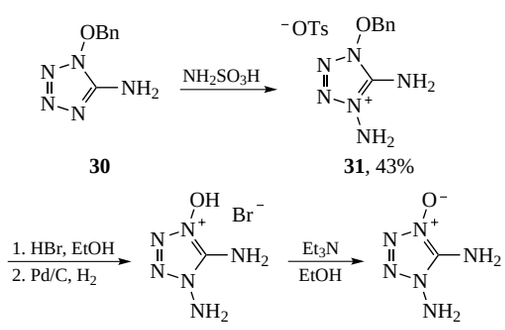


Scheme 8

hetaryl)furoxans. Thus formed azo-bridged (furoxanyl)azoles possess high densities and excellent detonation performance, although their mechanical sensitivities substantially depend on the presence of additional explosophores and range from primary to secondary explosives.[27,28]

Recently, our team reported a preparation of a series of highly energetic organic salts comprising the tetrazolylfuroxan anion, explosophoric azido or azo functionalities, and nitrogen-rich cations. [3 + 2] Cycloaddition of cyanofuroxans **21a**,**b** to NH_4N_3 generated *in situ* from $TMSN_3$ and NH_4F afforded tetrazolylfuroxan ammonium salts which were treated with $AgNO_3$ resulting in a formation of the corresponding silver salts **22a**,**b**. Subsequent metathesis reaction of silver salts **22a**,**b** with nitrogen-rich hydrochlorides successfully resulted in a series of energetic salts **23**–**28** (Scheme 8). Synthesized compounds exhibit good experimental densities (1.57–1.71 g cm^{-3}), very high enthalpies of formation (818–1363 kJ mol^{-1}), and, as a result, excellent detonation performance (D = 7.54–8.26 km s^{-1}, P = 23.4–29.3 GPa).[29]

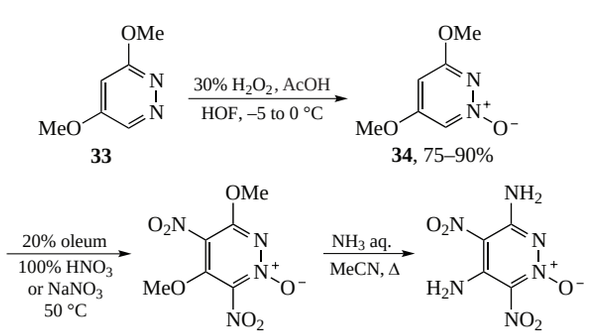
A rare example of energetic five-membered heterocyclic *N*-oxides involved the preparation of functionalized tetrazole-oxide derivative **29**. The tetrazole benzyl ether **30** was aminated using *O*-tosylhydroxylamine in a 1 : 1 $MeCN : CH_2Cl_2$ solution. Tosylate anion in 4-benzyloxy-1,5-diaminotetrazolium tosylate **31** was exchanged with a bromide one followed by debenzylation procedure to afford salt **32**. Subsequent base treatment of salt **32** afforded target energetic compound **29** in a moderate yield (Scheme 9).[30]



Scheme 9

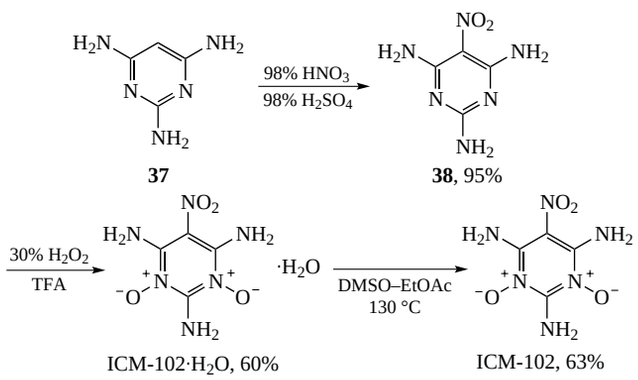
3. Monocyclic six-membered heterocyclic *N*-oxides

An introduction of the *N*-oxide functionality to the six-membered heterocyclic core is usually achieved by a direct oxidation of the ring nitrogens, although the presence of additional electron-withdrawing explosophoric groups requires the utilization of strong oxidizers. For example, oxidation of 3,5-dimethoxypyridazine **33** with H_2O_2 or HOF was successfully accomplished with a good yield of the corresponding *N*-oxide **34**. The presence of the electron-donating methoxy groups enabled subsequent nitration with 20% oleum and 100% nitric acid or $NaNO_3$ providing 3,5-dimethoxy-4,6-dinitropyridazine 1-oxide **35**. The second nitro group was able to be introduced only when the *N*-oxide was present within the heterocyclic core. Treatment of compound **35** with ammonia afforded energetic derivative **36** (Scheme 10).[31] Compound **35** may also be used as a starting material for further functionalization of the pyridazine scaffold, in particular, for an incorporation of *N*-methyl-*N*-nitro explosophoric moiety.[32]



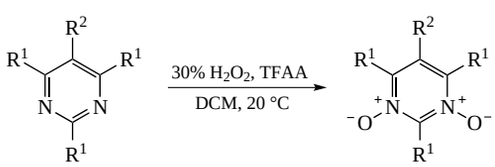
Scheme 10

One of the leading energetic materials, ICM-102, was recently synthesized by a three-step conversion of the commercially available 2,4,6-triaminopyrimidine **37**. Substrate **37** was nitrated to the corresponding 5-nitro derivative **38**, which was further oxidized to the corresponding dioxide isolated as a monohydrate. Dehydration was performed upon heating the obtained monohydrate in DMSO at 130 °C with subsequent dilution with EtOAc (Scheme 11). ICM-102 exhibits high experimental density (1.95 g cm^{-3}), high thermal decomposition temperature (284 °C) and superior detonation velocity (D = 9.2 km s^{-1}).[33]



Scheme 11

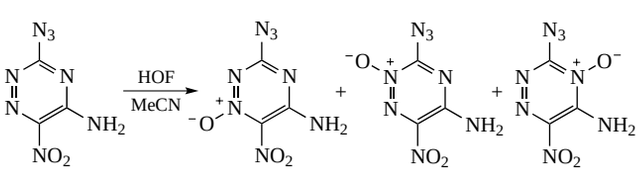
Later, some investigations on a preparation of energetic materials similar to ICM-102 were conducted. Functionalized pyrimidine precursors **39a**–**c** were oxidized to the corresponding dioxides **40a**–**c** with 30% H_2O_2 and TFAA in DCM at 20 °C (Scheme 12). Synthesized compounds are quite stable and insensitive to impact and exhibit good physicochemical properties (D = 9.4 km s^{-1}, P = 32 GPa).[34]



a R^1 = $NHNH_2$, R^2 = H
b R^1 = $NHNH_2$, R^2 = NO_2
c R^1 = N_3, R^2 = NO_2

Scheme 12

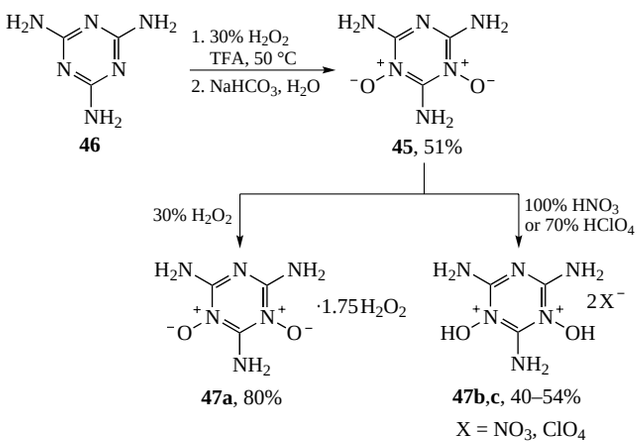
Oxidation of 3,5-diamino-6-nitro-1,2,4-triazine with Oxone selectively afforded 2-oxide derivative, albeit in a moderate yield.[35] On the contrary, oxidation of 5-amino-3-azido-6-nitro-1,2,4-triazine **41** with HOF resulted in a formation of three regioisomeric *N*-oxides **42**–**44** in nearly equimolar amounts



Scheme 13

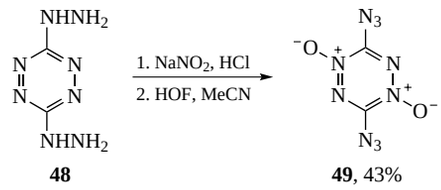
(Scheme 13). All three compounds possess detonation parameters between PETN and RDX. Of the three isomers, 2-oxide **43** has the highest detonation performance (D = 8.7 km s^{-1}, P = 31.8 GPa), while properties of regio-isomers **42** and **44** are somewhat lower (D = 8.6 km s^{-1}, P = 30.7–31.0 GPa).[36]

A promising approach for the design of *N*-oxide-derived hybrid oxidizing explosive based on a self-assembly of energetic molecules was recently developed. Using molecular electrostatic potential and proton affinities calculations, 2,4,6-triamino-1,3,5-triazine-1,3-dioxide **45** was rationally designed and synthesized *via* an oxidation of the commercially available melamine **46** (Scheme 14). Subsequent intermolecular assembly of compound **45** with several oxidants (H_2O_2, HNO_3 and $HClO_4$) afforded corresponding energetic materials **47a**–**c** which possess high densities, excellent detonation performance and acceptable mechanical sensitivities enabling their application potential as solid rocket propellants.[37]



Scheme 14

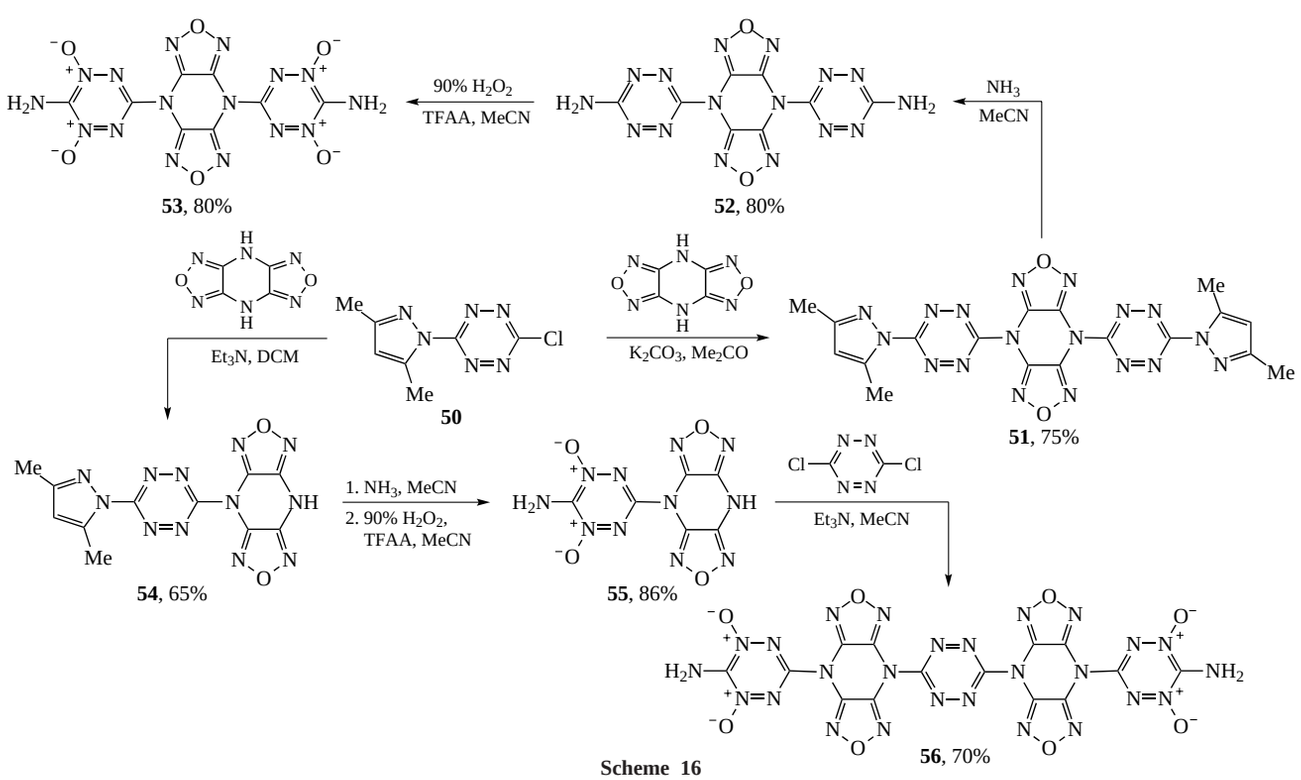
3,6-Dihydrazino-1,2,4,5-tetrazine **48** was used as a substrate in tandem nitrosation–oxidation sequence affording quite sensitive 3,6-diazido-1,2,4,5-tetrazine 1,5-dioxide **49**. Oxidation step can be performed using either HOF or a combination of H_2O_2 and TFA (Scheme 15).[38] Dioxide **49** has outstanding calculated detonation performance (D = 10.0 km s^{-1}, P = 45.8 GPa) which is close to that reported for 4,4′-dinitro-3,3′-diazenofuroxan – one of the most powerful CNO explosives ever reported.[39,40]



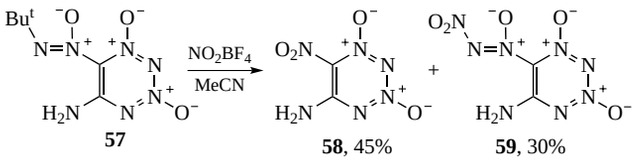
Scheme 15

Amino-1,2,4,5-tetrazines are excellent substrates for *N*-oxide formation with a variety of oxidizing reagents. Nucleophilic substitution of the chlorine atom in the corresponding tetrazine derivative **50** using 4*H*,8*H*-difurazano[3,4-*b*:3′,4′-*e*]pyrazine as a nucleophile in the presence of K_2CO_3 as a base afforded bifunctionalized product **51**. Subsequent treatment of compound **51** with ammonia resulted in a replacement of both dimethylpyrazolyl fragments and then both tetrazine rings in derivative **52** were chemoselectively oxidized to the corresponding tetra-*N*-oxide **53** (Scheme 16). Interestingly, a utilization of Et_3N in the reaction of chlorotetrazine **50** with difurazanopyrazine promoted the formation of the mono-substituted product **54**. Analogous conversion of the (dimethyl-pyrazolyl)tetrazine motif to the aminotetrazinedi-*N*-oxide one was achieved in a high yield. Finally, compound **55** was coupled with 3,6-dichlorotetrazine to afford polycyclic material **56**. Overall, compounds **53** and **56** displayed good detonation performance (D = 8.7–8.8 km s^{-1}, P = 32–33 GPa) similar to that of RDX, while exhibiting much better insensitivity.[41]

Nitration of pre-functionalized (*tert*-butyl-*NNO*-azoxy)-tetrazine **57** with an excess of NO_2BF_4 resulted in a mixture of nitro and (nitro-*NNO*-azoxy)tetrazines **58** and **59** (Scheme 17). This result confirms an ability of nitronium cation to promote destructive nitration of both *tert*-butyl and (*tert*-butyl-*NNO*-



Scheme 16



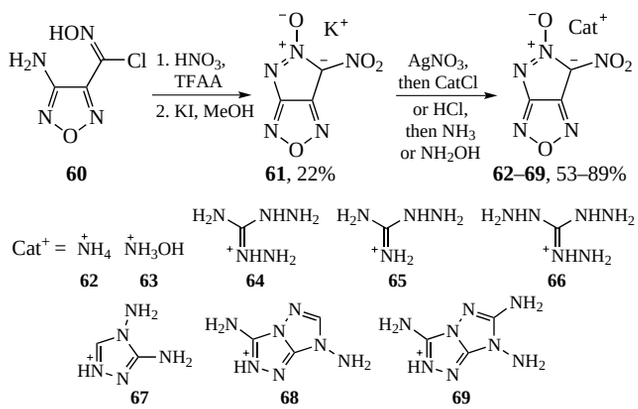
57 **58**, 45% **59**, 30%

Scheme 17

azoxy) groups. (Nitro-*NNO*-azoxy) compound **59** was obtained for the first time and is considered as potential energetic material.[42]

4. 5/5-Fused biheterocyclic *N*-oxides

A number of newly synthesized energetic materials incorporates a biheterocyclic (5/5 or 5/6) core possessing at least one *N*-oxide functionality. For example, an unusual intramolecular cyclization was observed upon nitration of chloroxime **60** with a mixture of 100% HNO_3 and TFAA followed by *in situ* reduction. Thus, a new fused high-energy potassium salt **61** bearing 6-nitropyrazolo[3,4-*c*]furazanate 5-oxide anion was prepared. Starting from compound **61** a series of energetic salts **62–69** incorporating high-nitrogen cations was obtained (Scheme 18). Hydroxylammonium salt **63** has the highest detonation performance but high mechanical sensitivity, which restricts its applicability.[43]



60 **61**, 22% **62–69**, 53–89%

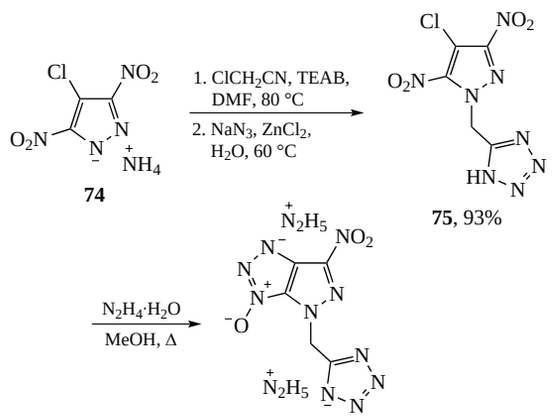
62 **63** **64** **65** **66**

67 **68** **69**

Scheme 18

Nitration of diaminofurazan **70** in 70% HNO_3 at 25 °C gave dinitramine, that is suitable for further cyclization conducted in Ac_2O medium in the presence of 1 equiv. of 93% H_2SO_4 to form a 1,2,3-triazole 2-oxide ring *via* generation of oxodiazonium ion. Thus formed potassium salt **71** was acidified using ion-exchange resins to the NH-form **72** which was further neutralized to produce ammonium and hydrazinium salts **73a**,**b**. Alternatively, double metathesis procedure may be applied to convert potassium salt **71** to the corresponding hydroxylammonium and triaminoguanidinium salts **73c**,**d** (Scheme 19). High detonation performance (D = 8.9–9.3 km s^{-1}, P = 34–43 GPa) along with elevated specific impulses enable potential application of these compounds as solid composite propellants.[44]

A new example of 5/5 fused biheterocyclic *N*-oxide-based energetic scaffold comprising the pyrazole and 1,2,3-triazole 1-oxide was recently synthesized. Initially, ammonium pyrazolate **74** was alkylated with chloroacetonitrile followed by [3 + 2] cycloaddition to assembly a tetrazole ring linked to the pyrazole one *via* methylene bridge. Reaction of compound **75** with hydrazine hydrate in refluxing methanol resulted in a formation of fused heterocyclic *N*-oxide **76** (Scheme 20).[45]



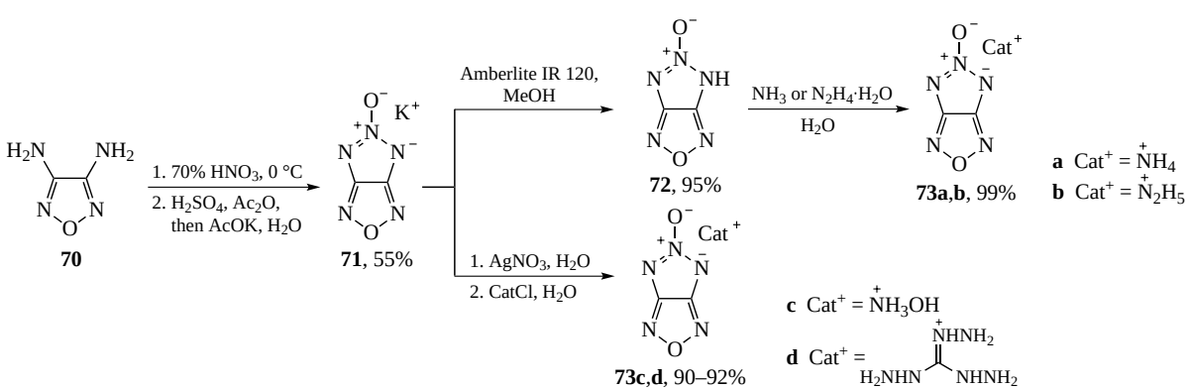
74 **75**, 93% **76**, 81%

Scheme 20

5. 5/6-Fused biheterocyclic *N*-oxides

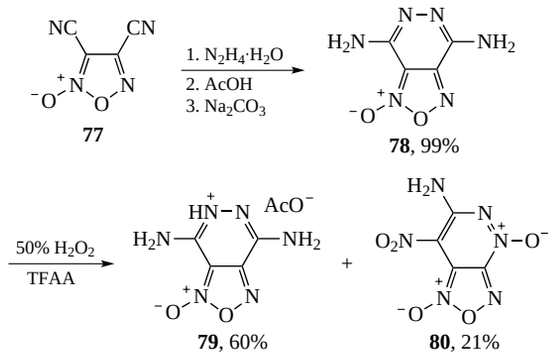
Regarding energetic condensed biheterocyclic scaffolds possessing at least one *N*-oxide functionality, serious advances were achieved in a series of 5/6 fused frameworks. For example, an interaction of dicyanofuroxan **77** with hydrazine hydrate followed by acid–base treatment afforded pyridazino[4,5-*c*]-furoxan **78**, which upon oxidation provided a mixture of protonated pyridazine **79** and di-*N*-oxide derivative **80** (Scheme 21). Utilization of HOF resulted in a cleavage of the pyridazine ring. Compound **80** displayed an energetic performance compared to triaminotrinitrobenzene (TATB) and insensitivity to mechanical stimuli. Such desired combination of properties makes di-*N*-oxide **80** a promising secondary explosive, attractive for high-performance applications.[46]

The construction of the fused-ring 2D structure is a very powerful way to balance the contradicting energy and safety properties of energetic materials. For example, diazotization of functionally substituted *NH*-azoles **81a–c** bearing vicinal amidoxime and amino moieties proceeded chemoselectively and resulted in an intramolecular azo coupling affording a series of 1,2,3-triazine 1-oxide fused biheterocyclic systems **82a–c**.



70 **71**, 55% **72**, 95% **73a**,**b**, 99% **73c**,**d**, 90–92%

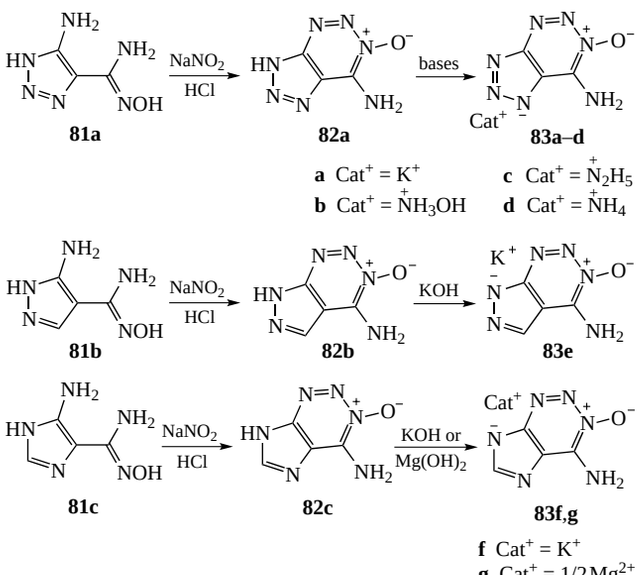
Scheme 19



77 **78**, 99% **79**, 60% **80**, 21%

Scheme 21

Neutralization of compounds **82a**–**c** afforded a series of energetic salts **83a**–**g** (Scheme 22).[47] Surprisingly, synthesized energetic materials also possessed fluorescent properties: most of these biheterocyclic systems are yellow solids which become green fluorescent materials under UV light (365 nm). Interestingly, thermal stabilities of NH-forms **82a**–**c** were generally higher than those of the corresponding salts **83**. Synthesized energetic materials exhibited good detonation velocities ranging from 6.9 km s^{-1} for **83f** to 9.4 km s^{-1} for **83c**, while all compounds were insensitive to friction. Later, this synthetic approach was expanded on a broad series of 1,2,3-triazine 1-oxides fused with aromatic and heteroaromatic motifs, although diazotization of diazine derivatives (pyridazine, pyrimidine and pyrazine) did not result in a formation of the target biheterocyclic core, but provided corresponding chloroximes as sole products.[48]



81a **82a** **83a**–**d**

a $Cat^+ = K^+$ **c** $Cat^+ = N_2H_5^+$

b $Cat^+ = NH_3OH^+$ **d** $Cat^+ = NH_4^+$

81b **82b** **83e**

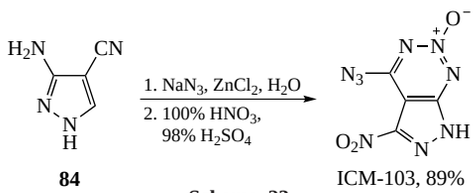
81c **82c** **83f**,**g**

f $Cat^+ = K^+$

g $Cat^+ = 1/2\,Mg^{2+}$

Scheme 22

Recently, a novel primary nitrogen-rich explosive ICM-103 was prepared *via* two-step transformation of 3-amino-4-cyanopyrazole **84** (Scheme 23). This approach involved a preliminary construction of the tetrazole ring by the reaction of substrate **84** with NaN_3 with subsequent nitration resulting in a cleavage of the tetrazole ring and recyclization to the

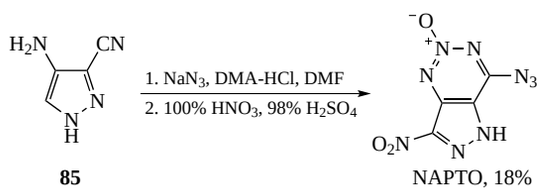


84 ICM-103, 89%

Scheme 23

1,2,3-triazine 2-oxide. ICM-103 is thermally stable up to 160 °C and meets all the industrially desired criteria for green primary explosives, including low-cost production and easy production scalability, high priming ability and reasonable flow ability.[49]

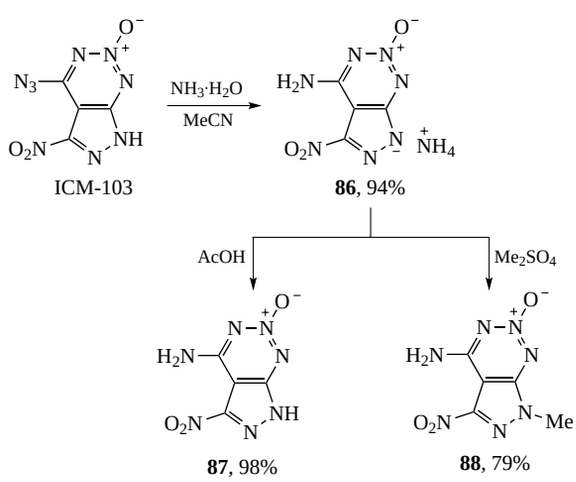
Regioisomeric to ICM-103 4-nitro-7-azidopyrazolo[3,4-*d*]-[1,2,3]triazine 2-oxide (NAPTO) was prepared in a similar manner starting from 4-amino-3-cyanopyrazole **85** (Scheme 24). NAPTO has higher onset decomposition temperature (203 °C) than ICM-103 and surprisingly low sensitivities to external stimuli. High insensitivity of NAPTO is attributed to its graphite-like molecular structure stabilized by hydrogen bonds dipole–dipole inductions. As a result, NAPTO exhibits an ultraflat 2D layered structure defined by a tight π–π stacking between layers with a considerably short layer spacing of 2.883 Å enabling sliding and compression between layers to absorb mechanical energy.[50] Taking into account high detonation performance of NAPTO (D = 9.1 km s^{-1}, P = 35.1 GPa), its application potential as powerful energetic material is quite high.



85 NAPTO, 18%

Scheme 24

Later,[51,52] substitution of the azido group in ICM-103 and NAPTO with an amino one afforded insensitive biheterocyclic energetic materials. In the case of transformations of ICM-103 the resulted ammonium salt **86** was further acidified to the corresponding NH-form **87** or chemoselectively methylated using Me_2SO_4 (Scheme 25).[52] Synthesized compounds **87** and **88** are classified as heat-resistant explosives due to their significantly high decomposition temperatures (348–365 °C). Moreover, energetic materials **87** and **88** exhibit good detonation performances (D = 8.1–8.5 km s^{-1}, P = 25.0–29.4 GPa) and low mechanical sensitivities. These results additionally support the necessity to finely tune molecular structure aiming to obtain promising energetic materials with a required set of properties (high heat resistance and low sensitivity in this case).



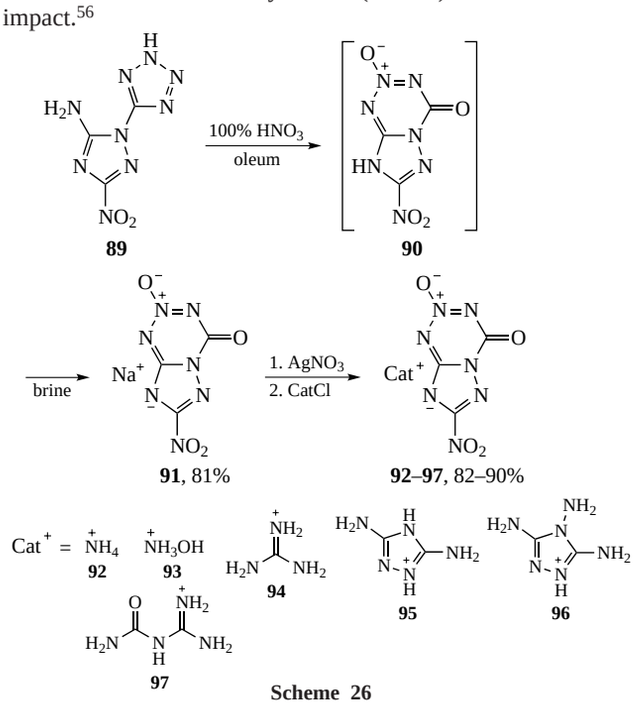
ICM-103 **86**, 94%

87, 98% **88**, 79%

Scheme 25

The formation of fused 1,2,3-triazine 2-oxides *via* exhaustive nitration of (het)arenes bearing vicinal amino and tetrazole motifs was found to be a general case for various substrates, albeit an introduction of diazine derivatives provided only corresponding nitramines.[48] Nitration of (1,2,4-triazolyl)-tetrazole **89** afforded a unique biheterocyclic structure of

7-nitro-4-oxo-4,8-dihydro[1,2,4]triazolo[5,1-*d*][1,2,3,5]-tetrazine 2-oxide **90**, which upon treatment with brine formed the corresponding sodium salt **91**. Tandem metathesis protocol applied to compound **91** afforded a series of nitrogen-rich energetic salts **92**–**97** (Scheme 26). All of the energetic salts **92**–**97** are stable and decompose above 230 °C and tend to be insensitive to impact, friction and electrostatic discharge. Detonation performance calculations for the energetic salts provide detonation pressures and velocities within the ranges 25.2–39.5 GPa and 7.9–9.1 km s^{-1}, respectively.[53,54] In a similar manner, a series of 7,8-dinitro-4-oxo-4,6-dihydropyrazolo-[5,1-*d*][1,2,3,5]tetrazine 2-oxide energetic salts was prepared, although their energetic properties were generally lower.[55] However, recently synthesized biheterocyclic derivative of 4-oxo-4,6-dihydro-3*H*-pyrazolo[3,4-*d*][1,2,3]triazine 2-oxide was found to be thermally stable (302 °C) and insensitive to impact.[56]



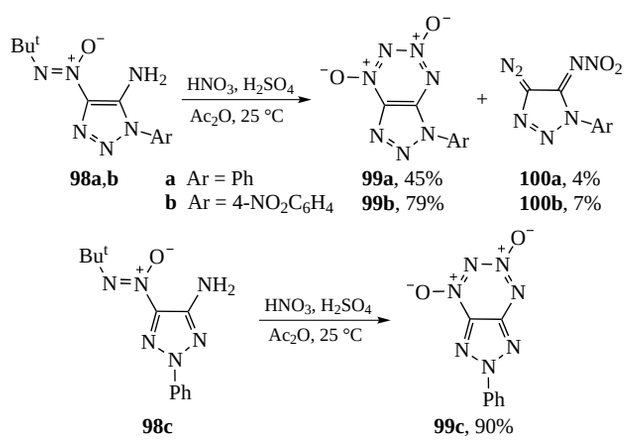
89 **90** **91**, 81% **92**–**97**, 82–90%

92 **93** **94** **95** **96** **97**

Scheme 26

Nitration of amino-1,2,3-triazoles **98a**–**c** bearing vicinal amino and *tert*-butyl-*NNO*-azoxy functionalities resulted in a formation of [1,2,3]triazolo[4,5-*e*][1,2,3,4]tetrazine 4,6-dioxides **99a**–**c**. In the case of 1-aryl-1*H*-1,2,3-triazoles **99a**,**b**, diazo-nitroimines **100a**,**b** were also isolated as by-products (Scheme 27).[57]

Interesting representatives of tetraazapentalenes *via* transformations of [1,2,3]triazolo[4,5-*e*][1,2,3,4]tetrazine

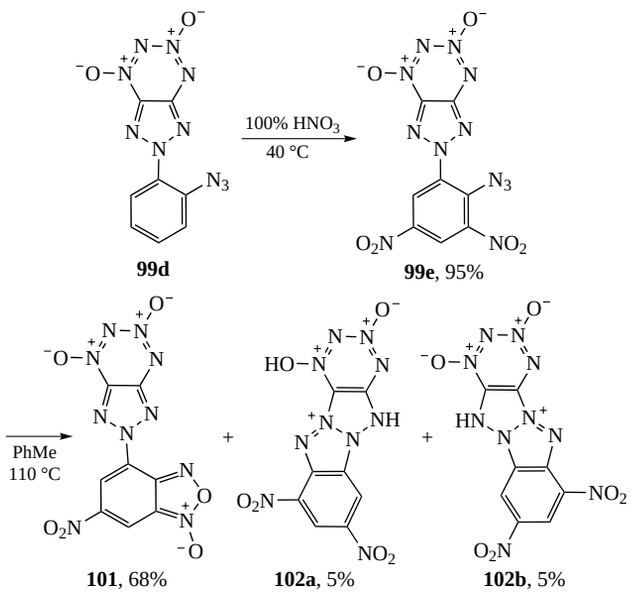


98a,**b** **a** Ar = Ph **b** Ar = 4-$NO_2C_6H_4$ **99a**, 45% **99b**, 79% **100a**, 4% **100b**, 7%

98c **99c**, 90%

Scheme 27

4,6-dioxides were synthesized. Nitration of *o*-azidophenyl substituted derivative **99d** afforded multi-functionalized arene **99e** which underwent thermal intramolecular cyclization to form benzofuroxan **101**. Tetraazapentalenes **102a** and **102b** were formed as by-products in equal proportions and in low yields (Scheme 28). Compound **101** may be of interest as an energetic material due to a combination of good thermal stability (190 °C), high calculated enthalpy of formation (1005 kJ mol^{-1}) and good density (1.84 g cm^{-3}).[58(*a*)] Later, the same research group developed a more useful approach toward the construction of tetraazapentalenes *via* thermolysis of the corresponding *o*-azidophenyl[1,2,3]triazolo[4,5-*e*][1,2,3,4]tetrazine 4,6-dioxides in *o*-dichlorobenzene.[58(*b*)]

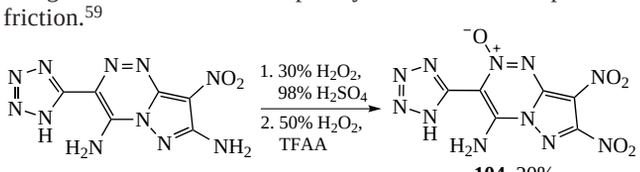


99d **99e**, 95%

101, 68% **102a**, 5% **102b**, 5%

Scheme 28

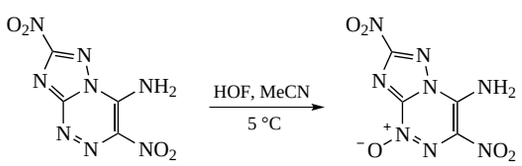
In addition to the above-mentioned substrate-specific approaches common oxidation protocols were used in the chemistry of 5/6 fused biheterocyclic systems to prepare corresponding energetic *N*-oxides. For example, oxidation of pyrazolo[5,1-*c*][1,2,4]triazine **103** enabled stepwise installation of nitro group and *N*-oxide functionality to the biheterocyclic core (Scheme 29). Although thus formed *N*-oxide **104** has lower onset decomposition temperature (273 °C) than parent compound **103** (335 °C), it has higher detonation velocity (D = 8.9 km s^{-1} for **104** *vs*. 8.7 km s^{-1} for **103**), while both energetic materials are completely insensitive to impact and friction.[59]



103 **104**, 20%

Scheme 29

High-energy scaffold **105** was chemoselectively oxidized to 4-amino-3,7-dinitrotriazolo[5,1-*c*][1,2,4]triazine 4-oxide **106** (Scheme 30). Compound **106** has moderate thermal stability

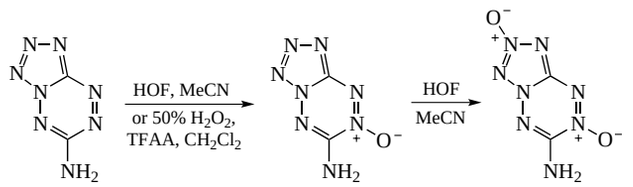


105 **106**, 80%

Scheme 30

(138 °C), acceptable mechanical sensitivities and high detonation performance (D = 9.0 km s^{-1}, P = 35.4 GPa).[60]

The same reaction conditions were appropriate for an oxidation of 6-amino[1,5-*b*]tetrazolo-1,2,4,5-tetrazine **107**, which can be selectively oxidized to mono-*N*-oxide **108** and further to di-*N*-oxide **109** (Scheme 31). Energetic material **109** has moderate thermal stability (150 °C), but outstanding calculated detonation performance (D = 9.6 km s^{-1}, P = 41.3 GPa).[38] For similar oxidation of 3,6-diamino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine a combination of H_2O_2 and TFAA was used.[61]

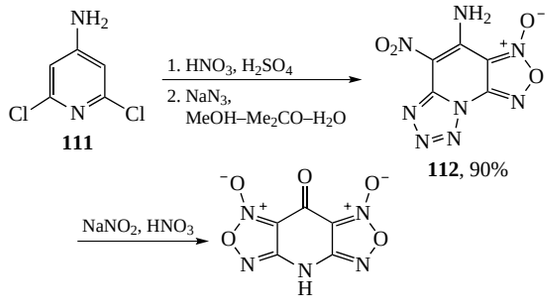


107 **108**, 42% **109**, 70%

Scheme 31

6. Tri- and tetraheterocyclic *N*-oxides

Tri- and tetraheterocyclic systems bearing *N*-oxide functionality are rarely considered as promising energetic compounds. However, recent investigations in this area gained some novel insights into the chemistry and performance of energetic materials. In particular, an operationally simple and scalable protocol for the three-step synthesis of 4*H*,8*H*-bis-furazano[3,4-*b*:3′,4′-*e*]pyridin-8-one 1,7-dioxide **110** from commercially available 4-amino-2,6-dichloropyridine **111** was developed. This method is based on nitration of substrate **111** followed by azidation to form triheterocyclic system **112** (Scheme 32). Introduction of compound **112** into nitrosation–nitration process resulted in a cleavage of the tetrazole ring due to the azide–tetrazole tautomerism with subsequent cyclization of vicinal azido and nitro groups into another furoxan ring, while amino group underwent diazotization with subsequent hydrolysis. Compound **110** represents new heterocyclic system



111 **112**, 90%

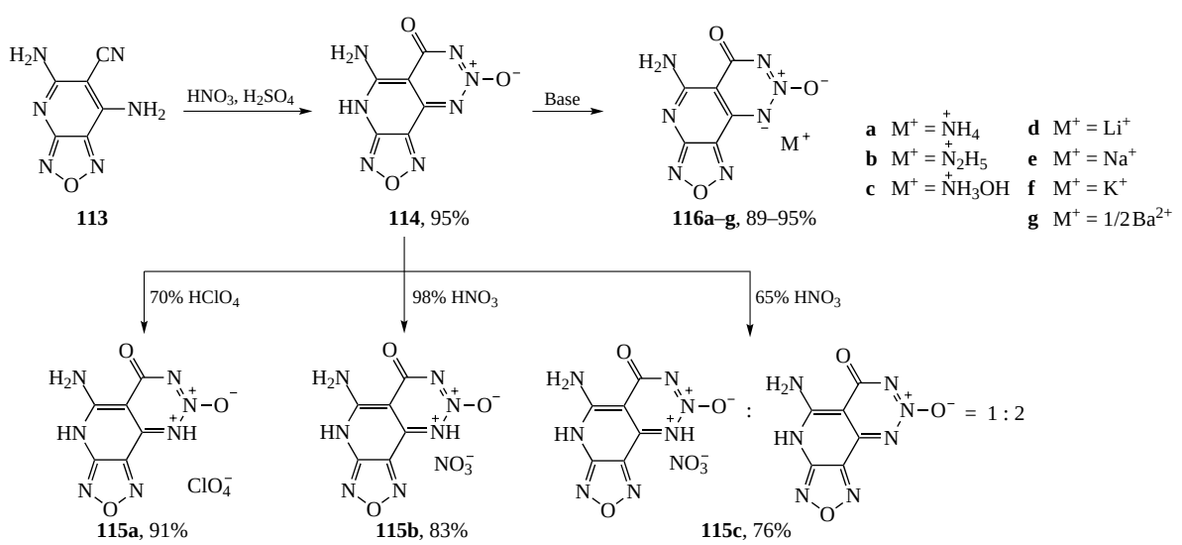
110, 71%

Scheme 32

and displays high density (1.925 g cm^{-3}), acceptable thermal stability (184 °C) and good detonation performance (D = 8.5 km s^{-1}, P = 33.6 GPa) superior to that of NTO (D = 8.4 km s^{-1}, P = 32.3 GPa).[62]

Nitration of functionalized biheterocyclic substrate **113** resulted in an assembly of the 1,2,3-triazine 2-oxide ring in nearly quantitative yield of compound **114**. Structure **114** is arguably the first fused amphoteric energetic molecule that can be protonated and deprotonated by acids and bases to obtain its cationic **115a–c** and anionic salts **116a–g** (Scheme 33). Compound **114** and all its energetic salts exhibited very good thermal stabilities with onset decomposition temperatures ranging from 310 °C for **116b** to 344 °C for **116d**. Due to the coplanar polycyclic structure, synthesized salts feature considerably high enthalpies of formation (1.3–2.4 kJ g^{-1}) and ring-strain energy stored in the molecules enabling their application potential as heat-resistance energetic materials.[63]

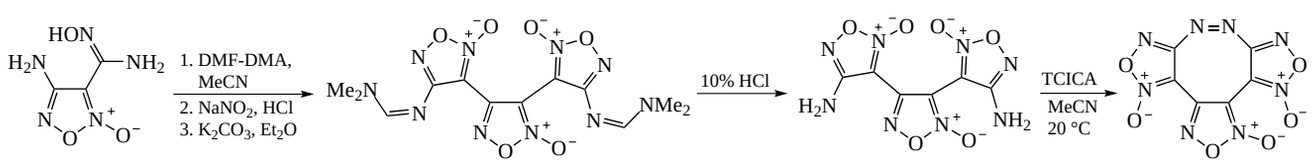
Three-step transformation of (furoxanyl)amidoxime **117** afforded terfuroxan **118**, which underwent acid-promoted deprotection of the amino groups to the corresponding diamine **119**. Intramolecular oxidative cyclization of compound **119** using trichloroisocyanurate (TCICA) resulted in a formation of diazocine **120** fused with three furoxan rings (Scheme 34). Compound **120** exhibits high density (1.895 g cm^{-3}) and is thermally stable up to 161 °C. Along with a zero oxygen balance



113 **114**, 95% **116a–g**, 89–95%

115a, 91% **115b**, 83% **115c**, 76%

Scheme 33



117 **118**, 67% **119**, 55% **120**, 64%

Scheme 34

and superior detonation performance (D = 9.4 km s^{-1}, P = 39.6 GPa) as well as reasonable sensitivities, this energetic material demonstrates a promising application potential.[64]

7. Summary and outlook

In conclusion, the main achievements in the design and synthesis of heterocyclic *N*-oxide-based high-energy materials reported within last five years were highlighted. Various routes to the synthesis, functionalization and structural diversification of 5- and 6-membered heterocyclic *N*-oxides along with their 5/5 and 5/6 fused systems were discussed.

Aromatic heterocyclic *N*-oxides retain leading position as valuable building blocks for the preparation of various energy-rich materials. Due to the planarity, high nitrogen–oxygen content and optimal crystal packing, heterocyclic *N*-oxides may serve as a synthetic platform for the construction of wide arrays of structurally diverse energy-rich derivatives with good detonation performance. Most of the monocyclic *N*-oxides possess quite high mechanical sensitivities, which defines their application potential as promising primary explosives. At the same time, to reduce the sensitivity to impact and friction, synthesis of fused nitrogen-rich bi-, tri- and tetraheterocyclic compounds bearing at least one *N*-oxide moiety was extensively performed in recent years. From the synthetic chemistry point of view, common condensation or direct oxidation protocols were applied quite often to prepare target heterocyclic systems and to install *N*-oxide functionality. In addition, very useful methods for an assembly of the 1,2,3-triazine oxide core *via* diazotization or nitration of 1,2-difunctionalized (het)arenes bearing amino group and amidoxime functionality or a tetrazole ring were developed. This approach was found to be a powerful tool to construct promising low sensitive or completely insensitive energetic materials with good detonation performance and, in particular cases, high thermal stability. Such balanced properties are of paramount importance to unlock application potential of these heterocyclic systems as multipurpose energetic materials.

Taking into account the emerging development of heterocyclic chemistry, there is no doubt that heterocyclic *N*-oxide-based energetic materials will retain their leading position in the framework of materials science. In our opinion, a search for prospective high-energy materials in this series is far from being exhausted. A combined multidisciplinary investigation will gain deep insights in structure–property relationships and will also provide new industrial applications.

This work was supported by the Russian Science Foundation (grant no. 19-73-20074).

References

1 J. Zhou, J. Zhang, B. Wang, L. Qiu, R. Xu and A. B. Sheremetev, *FirePhysChem*, 2022, **2**, 83.
2 O. T. O'Sullivan and M. J. Zdilla, *Chem. Rev.*, 2020, **120**, 5682.
3 L. L. Fershtat and N. N. Makhova, *ChemPlusChem*, 2020, **85**, 13.
4 I. V. Kuchurov, M. N. Zharkov, L. L. Fershtat, N. N. Makhova and S. G. Zlotin, *ChemSusChem*, 2017, **10**, 3914.
5 S. G. Zlotin, A. M. Churakov, M. P. Egorov, L. L. Fershtat, M. S. Klenov, I. V. Kuchurov, N. N. Makhova, G. A. Smirnov, Yu. V. Tomilov and V. A. Tartakovsky, *Mendeleev Commun.*, 2021, **31**, 731.
6 (*a*) P. Yin and J. M. Shreeve, *Adv. Heterocycl. Chem.*, 2017, **121**, 89; (*b*) H. Gao, Q. Zhang and J. M. Shreeve, *J. Mater. Chem. A*, 2020, **8**, 4193.
7 N. E. Leonov, S. E. Semenov, M. S. Klenov, A. M. Churakov, Yu. A. Strelenko, A. N. Pivkina, I. V. Fedyanin, D. B. Lempert, T. S. Kon'kova, Yu. N. Matyushin, E. A. Miroshnichenko and V. A. Tartakovsky, *Mendeleev Commun.*, 2021, **31**, 789.
8 N. E. Leonov, F. M. Sidorov, M. S. Klenov, A. M. Churakov, Yu. A. Strelenko, A. N. Pivkina, I. V. Fedyanin, D. B. Lempert, T. S. Kon'kova, Yu. N. Matyushin and V. A. Tartakovsky, *Mendeleev Commun.*, 2021, **31**, 792.
9 D. B. Vinogradov, P. V. Bulatov, E. Yu. Petrov and V. A. Tartakovsky, *Mendeleev Commun.*, 2021, **31**, 795.
10 D. E. Chavez, *Top. Heterocycl. Chem.*, 2017, **53**, 1.
11 L. L. Fershtat and F. E. Teslenko, *Synthesis*, 2021, **53**, 3673.
12 N. N. Makhova, L. I. Belen'kii, G. A. Gazieva, I. L. Dalinger, L. S. Konstantinova, V. V. Kuznetsov, A. N. Kravchenko, M. M. Krayushkin, O. A. Rakitin, A. M. Starosotnikov, L. L. Fershtat, S. A. Shevelev, V. Z. Shirinian and V. N. Yarovenko, *Russ. Chem. Rev.*, 2020, **89**, 55.
13 D. M. Bystrov, L. L. Fershtat and N. N. Makhova, *Chem. Heterocycl. Compd.*, 2019, **55**, 1143.
14 N. N. Makhova and L. L. Fershtat, *Tetrahedron Lett.*, 2018, **59**, 2317.
15 N. N. Makhova and L. L. Fershtat, in *Comprehensive Heterocyclic Chemistry IV*, Elsevier, Amsterdam, 2022, vol. 5, p. 190.
16 L. Zhai, J. Zhang, M. Wu, H. Huo, F. Bi and B. Wang, *J. Mol. Struct.*, 2020, **1222**, 128934.
17 L. L. Fershtat, I. V. Ovchinnikov, M. A. Epishina, A. A. Romanova, D. B. Lempert, N. V. Muravyev and N. N. Makhova, *ChemPlusChem*, 2017, **82**, 1315.
18 A. A. Larin, A. V. Shaferov, K. A. Monogarov, D. B. Meerov, A. N. Pivkina and L. L. Fershtat, *Mendeleev Commun*., 2022, **32**, 111.
19 A. A. Larin, A. V. Shaferov, M. A. Epishina, I. N. Melnikov, N. V. Muravyev, I. V. Ananyev, L. L. Fershtat and N. N. Makhova, *ACS Appl. Energy Mater*., 2020, **3**, 7764.
20 L. Zhai, F. Bi, Y. Luo, N. Wang, J. Zhang and B. Wang, *Sci. Rep.*, 2019, **9**, 4321.
21 Q. Yu, A. K. Chinnam, P. Yin, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2020, **8**, 5859.
22 L. Zhai, F. Bi, J. Zhang, J. Zhang, X. Li, B. Wang and S. Chen, *ACS Omega*, 2020, **5**, 11115.
23 L. Zhai, F. Bi, Y. Luo, L. Sun, H. Huo, J. Zhang, J. Zhang, B. Wang and S. Chen, *Chem. Eng. J.*, 2020, **391**, 123573.
24 E. C. Johnson, E. J. Bukowski, J. J. Sabatini, R. C. Sausa, E. F. C. Byrd, M. A. Garner and D. E. Chavez, *ChemPlusChem*, 2019, **84**, 319.
25 L. L. Fershtat, I. V. Ananyev and N. N. Makhova, *RSC Adv.*, 2015, **5**, 47248.
26 E. C. Johnson, J. J. Sabatini, D. E. Chavez, L. A. Wells, J. E. Banning, R. C. Sausa, E. F. C. Byrd and J. A. Orlicki, *ChemPlusChem*, 2020, **85**, 237.
27 H. Xiong, G. Cheng, Z. Zhang and H. Yang, *New J. Chem.*, 2019, **43**, 7784.
28 A. A. Larin, A. V. Shaferov, A. S. Kulikov, A. N. Pivkina, K. A. Monogarov, A. O. Dmitrienko, I. V. Ananyev, D. V. Khakimov, L. L. Fershtat and N. N. Makhova, *Chem. – Eur. J*., 2021, **27**, 14628.
29 A. A. Larin, N. V. Muravyev, A. N. Pivkina, K. Y. Suponitsky, I. V. Ananyev, D. V. Khakimov, L. L. Fershtat and N. N. Makhova, *Chem. – Eur. J*., 2019, **25**, 4225.
30 S. R. Yocca, M. Zeller, E. F. C. Byrd and D. G. Piercey, *J. Mater. Chem. A*, 2022, **10**, 1876.
31 I. Gospodinov, T. M. Klapötke and J. Stierstorfer, *Eur. J. Org. Chem*., 2018, 1004.
32 I. Gospodinov, J. Singer, T. M. Klapötke and J. Stierstorfer, *Z. Anorg. Allg. Chem*., 2019, **645**, 1247.
33 Y. Wang, Y. Liu, S. Song, Z. Yang, X. Qi, K. Wang, Y. Liu, Q. Zhang and Y. Tian, *Nat. Commun.*, 2018, **9**, 2444.
34 A. K. Yadav, V. D. Ghule and S. Dharavath, *J. Mater. Chem. A*, 2022, **10**, 12702.
35 S. E. Creegan, M. Zeller, E. F. C. Byrd and D. G. Piercey, *Cryst. Growth Des*., 2021, **21**, 3922.
36 S. E. Creegan, M. Zeller, E. F. C. Byrd and D. G. Piercey, *Propellants, Explos. Pyrotech*., 2021, **46**, 214.
37 S. Song, Y. Wang, W. He, K. Wang, M. Yan, Q. Yan and Q. Zhang, *Chem. Eng. J*., 2020, **395**, 125114.
38 D. E. Chavez, D. A. Parrish, L. Mitchell and G. H. Imler, *Angew. Chem., Int. Ed*., 2017, **56**, 3575.
39 I. V. Ovchinnikov, N. N. Makhova, L. I. Khmel'nitskii, V. S. Kuz'min, L. N. Akimova and V. I. Pepekin, *Dokl. Chem.*, 1998, **39**, 67.
40 A. A. Larin, D. M. Bystrov, L. L. Fershtat, A. A. Konnov, N. N. Makhova, K. A. Monogarov, D. B. Meerov, I. N. Melnikov, A. N. Pivkina, V. G. Kiselev and N. V. Muravyev, *Molecules*, 2020, **25**, 5836.
41 C. Snyder, L. Wells, D. Chavez, G. H. Imler and D. A. Parrish, *Chem. Commun*., 2019, **55**, 2461.
42 M. S. Klenov, N. E. Leonov, A. A. Guskov, A. M. Churakov, Yu. A. Strelenko and V. A. Tartakovsky, *Russ. Chem. Bull.*, 2019, **68**, 1798.
43 Y. Tang, C. He and J. M. Shreeve**,** *J. Mater. Chem. A*, 2017, **5**, 4314.

44 A. A. Voronin, I. V. Fedyanin, A. M. Churakov, A. N. Pivkina, N. V. Muravyev, Y. A. Strelenko, M. S. Klenov, D. B. Lempert and V. A. Tartakovsky, *ACS Appl. Energy Mater*., 2020, **3**, 9401.
45 D. Kumar, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Chem. – Eur. J*., 2017, **23**, 7876.
46 Y. Tang, C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Chem. – Eur. J*., 2017, **23**, 15022.
47 Y. Tang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *ACS Appl. Energy Mater*., 2019, **2**, 8871.
48 Y. Liu, X. Qi, W. Zhang, P. Yin, Z. Cai and Q. Zhang, *Org. Lett.*, 2021, **23**, 734.
49 M. Deng, Y. Feng, W. Zhang, X. Qi and Q. Zhang, *Nat. Commun*., 2019, **10**, 1339.
50 Y. Feng, M. Deng, S. Song, S. Chen, Q. Zhang and J. M. Shreeve, *Engineering*, 2020, **6**, 1006.
51 Y. Cao, Z. Cai, J. Shi, Q. Zhang, Y. Liu and W. Zhang, *Energ. Mater. Front.*, 2022, **3**, 26.
52 M. Deng, F. Chen, S. Song, S. Huang, Y. Wang and Q. Zhang, *Chem. Eng. J.*, 2022, **429**, 132172.
53 C. Bian, X. Dong, X. Zhang, Z. Zhou, M. Zhang and C. Li, *J. Mater. Chem. A*, 2015, **3**, 3594.
54 J. Wu, J. Xu, W. Li and H. Li, *Propellants, Explos. Pyrotech.*, 2020, **45**, 536.
55 B. Zhao, P. Wang, W. Fu, C. Li and Z. Zhou, *ChemistrySelect*, 2018, **3**, 4797.
56 C. Lei, G. Cheng, Z. Yi, Q. Zhang and H. Yang, *Chem. Eng. J.*, 2021, **416**, 129190.
57 A. A. Voronin, A. M. Churakov, M. S. Klenov, Y. A. Strelenko, I. V. Fedyanin and V. A. Tartakovsky, *Eur. J. Org. Chem*., 2017, 4963.
58 (*a*) A. O. Shvets, A. A. Konnov, M. S. Klenov, A. M. Churakov, Yu. A. Strelenko and V. A. Tartakovsky, *Russ. Chem. Bull.*, 2020, **69**, 739; (*b*) A. A. Konnov, M. S. Klenov, A. M. Churakov, Y. A. Strelenko, A. O. Dmitrienko, L. N. Puntus, K. A. Lyssenko and V. A. Tartakovsky, *Asian J. Org. Chem*., 2018, **7**, 2534.
59 Z. Cheng, Z. Zhang, Q. Ma, L. Yang, H. Yang, G. Cheng, G. Fan and W. Yang, *Chem. Eng. J.*, 2022, **436**, 131990.
60 D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler and D. A. Parrish, *Angew. Chem., Int. Ed*., 2016, **55**, 15315.
61 L. Hu, P. Yin, G. H. Imler, D. A. Parrish, H. Gao and J. M. Shreeve, *Chem. Commun*., 2019, **55**, 8979.
62 R. Z. Gilmanov, V. G. Nikitin, F. G. Khayrutdinov, K. V. Strizhenko, K. Yu. Suponitsky and A. B. Sheremetev, *Mendeleev Commun.*, 2022, **32**, 114.
63 L. Ding, P. Wang, Q. Lin, D. Li, Y. Xu and M. Lu, *Chem. Eng. J.*, 2022, **432**, 134293.
64 C. He, H. Gao, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2018, **6**, 9391.

Received: 9th September 2022; Com. 22/6995