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Advances in the chemistry of furazano[3,4-*b*]pyrazines and their analogues

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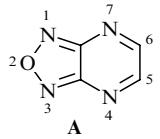
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Abstract. The published data on the methods for the synthesis of furazans fused to six-membered heterocycles with two heteroatoms in positions 1 and 4, their reactivities and practical applications are considered and systematised. The bibliography includes 89 references.

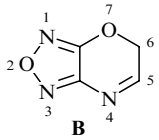
I. Introduction

The first paper devoted to the synthesis of compounds of the furazanopyrazine series was published in 1969.[1] However, intense development of this branch of chemistry began only in the mid-1980's when nitro derivatives of furazanopyrazines were recommended for use as explosives. High operating characteristics of this class of compounds attracted the attention of the specialists and gave impetus to comprehensive studies of their miscellaneous derivatives. Systematic studies of high-energy materials based on furazanopyrazine have led to the development of a vast variety of effective components of explosives and propellants. These studies provided profound insight into the chemistry and reactivities of furazanopyrazines and made accessible their polyfunctional derivatives. These achievements stimulated investigations into other properties of furazanopyrazines, *viz*., biological activity, photosensitivity, *etc*. Obviously, furazanopyrazine analogues where one or both pyrazine nitrogen atoms are replaced by oxygen or sulfur atoms are promising candidates for medicinal drugs. However, the methods for their synthesis are still poorly studied. The lack of efficient procedures for the preparation of such compounds impedes further investgations into their properties.

Four structural types in which the furazan (1,2,5-oxadiazole) ring is fused to a six-membered ring containing two heteroatoms in positions 1 and 4 are presently known, namely furazano[3,4-*b*]-pyrazine (**A**), furazano[3,4-*b*][1,4]oxazine (**B**), 1,4-dioxino[2,3-*c*]-furazan (**C**) and 1,4-dithiino[2,3-*c*]furazan (**D**).



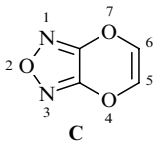
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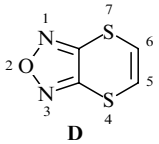
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C



D

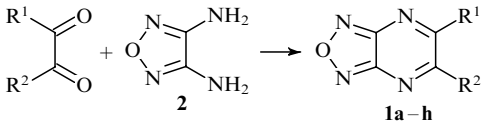
The presence of three contiguous heteroatoms in the furazan structure determines the pronounced electron-withdrawing character of this heterocycle. The bond localisation in the heterodiene fragment of furazan is strongly fixed; therefore, its derivatives are not prone to annular-group tautomerism. These features of the furazan ring determine the reactivities of all of its derivatives.[2–5]

This review is an attempt to generalise the whole body of available data on the synthesis, properties and applications of furazanopyrazines and their analogues. The review is intended mostly for organic chemists and is aimed at stimulating further studies in this field.

II. Furazano[3,4-*b*]pyrazine derivatives

1. Synthesis

The furazanopyrazine system can be built starting from furazan or pyrazine derivatives. Condensation of α-dicarbonyl compounds with aromatic and heterocyclic *o*-diamines is the most popular procedure for the synthesis of fused pyrazines. For the first time, this reaction was used for the preparation of furazanopyrazines **1** in 1969.[1] 3,4-Diaminofurazan (**2**) was used as a diamine.



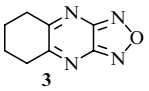
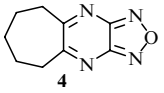
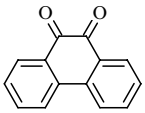
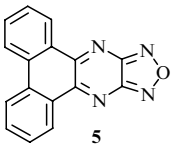
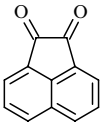
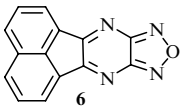
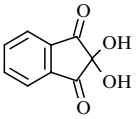
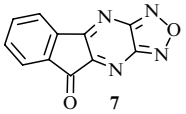
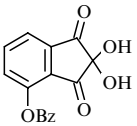
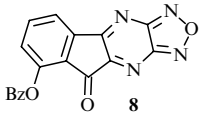
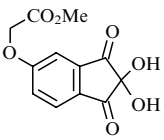
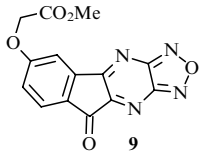
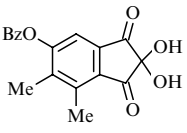
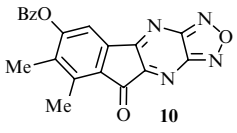
2 **1a – h**

Compound **1**	R^1	R^2	Reaction conditions	Yield (%)	Ref.
a	Ph	Ph	AcOH, 110 °C	35	1
	Ph	Ph	$BF_3 \cdot OEt_2$, 130 °C, 10 min	84	6
b	Me	Me	AcOH, 50 °C	51	7
c	Ph	H	AcOH, EtOH (1 : 3), Δ, 2 h	92	6
	Ph	H	AcOH, EtOH (1 : 1), Δ, 1 h	68	8
	Ph	H	AcOH, Δ, 2.5 h	53	9
d	4-ClC_6H_4	H	AcOH, EtOH (1 : 1), Δ, 1 h	69	8

Compound **1**	R^1	R^2	Reaction conditions	Yield (%)	Ref.
e	4-BrC_6H_4	H	AcOH, EtOH (1 : 1), Δ, 1 h	73	8
f	4-$MeOC_6H_4$	H	AcOH, EtOH (1 : 1), Δ, 1 h	65	8
g	4-$O_2NC_6H_4$	H	AcOH, EtOH (1 : 1), Δ, 1 h	78	8
h	Ph	Me	AcOH, EtOH (1 : 3), Δ, 2 h	79	6

The nucleophilicities of amino groups in compound **2** are much lower than those in aromatic *o*-diamines (*e.g.*, *o*-phenylenediamine); therefore, more drastic reaction conditions are required. Later, this method and its modifications were used for the synthesis of the furazano[3,4-*b*]pyrazine derivatives **1a**–**h**.[6–9]

Table 1. Reaction conditions and yields of the reaction products of cyclic α-diketones with the diamine **2**.

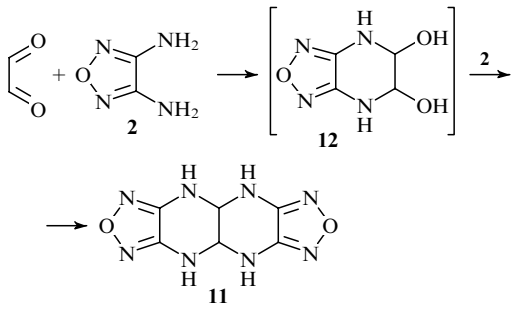
α-Diketone	Reaction conditions with the diamine **2**	Product	Yield (%)	Ref.
	AcOH,[a] EtOH, Δ, 1 h	 **3**	45	8
	AcOH,[a] EtOH, Δ, 1 h	 **4**	39	8
	AcOH, Δ	 **5**	60	1
	AcOH, Δ	 **6**	80	1
	EtOH, Δ, 10 min	 **7**	86 83	8 11
	AcOH,[a] EtOH, Δ, 6 h	 **8**	46	10
	AcOH,[a] EtOH, Δ, 4 h	 **9**	19	10
	AcOH,[a] EtOH, Δ, 4 h	 **10**	33	10

[a] AcOH : EtOH = 1 : 1.

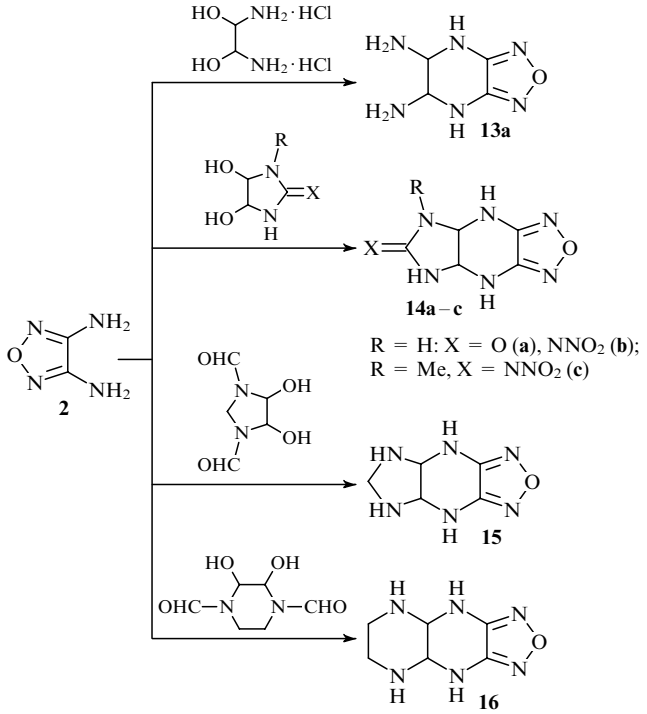
This reaction is carried out by heating the reactants in acetic acid or in a mixture of acetic acid and ethanol. The preparation of the derivative **1a** by melting of benzil with the diamine **2** in the presence of boron trifluoride etherate has been described.[6] Under these conditions, the target product was obtained in 84% yield after 10 min. However, this single example of the use of a Lewis acid as a promoter of this reaction does not allow one to judge on the applicability of this approach to other subjects.

Cyclic α-diketones react with the diamine **2** under similar conditions to yield polycyclic derivatives **3**–**10** (Table 1).[1,8,10,11]

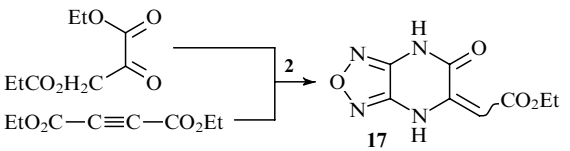
Glyoxal reacts with the diamine **2** in water in the presence of hydrochloric acid at 60 °C to give the tetracycle **11** in a quantitative yield.[12–17] The reaction proceeds *via* intermediate dihydroxy derivative **12**.



Preformed glyoxal adducts with NH_4Cl or weakly basic amines can be used in a reaction with diamine **2** in the presence of acids. This approach was used for the synthesis of partially hydrogenated furazanopyrazines **13**–**16**;[16,18,19] however, the yields of reaction products seldom exceeded 60%. Compound **14b** was obtained in 55% yield by condensation of the dihydroxy derivative **12** with nitroguanidine.[19]

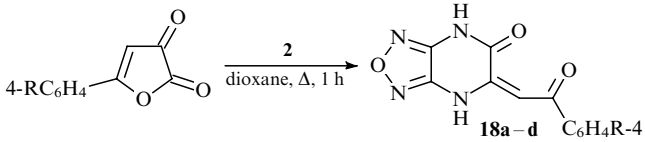


Heating of ethyl oxaloacetate with the diamine **2** for 1 h at 140–150 °C affords a mixture of *Z*,*E*-isomers of ethoxycarbonylmethylidene pyrazinone **17** (yield 54%).[20] If the condensation is carried out in boiling acetic acid, the product yield increases to 85%.[21] Pyrazinone **17** was also synthesised by boiling the amine **2** with diethyl acetylenedicarboxylate (AcOH, EtOH, 45 min; yield 74%).[8]



17

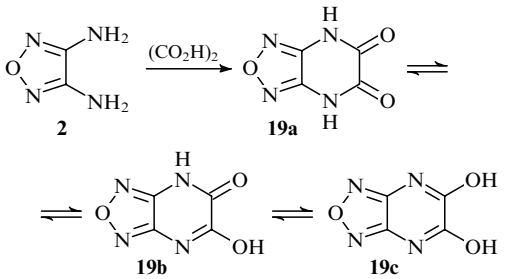
Cyclic α-keto ethers, *viz*., 2,3-dihydrofuran-2,3-diones, condense with the diamine **2** in boiling dioxane to yield pyrazinones **18a**–**d**. The nature of the substituent in the phenyl ring of the starting furandione does not influence the yields of reaction products which are in the range 60%–75%.[22,23]



18a–**d**

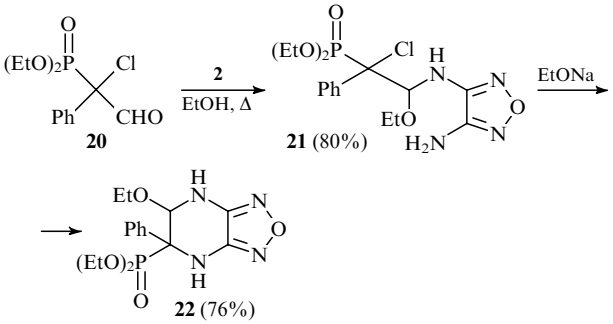
R = Me (**a**), Br (**b**), Cl (**c**), OMe (**d**).

In contrast to α-keto acids used in the form of esters for the preparation of hydrogenated furazanopyrazines (furazanopiperazines), oxalic acid reacts with the diamine **2** on boiling in dilute hydrochloric acid. The reaction product (yield 30%) exists as an equilibrium mixture of tautomers **19a**–**c**.[1]



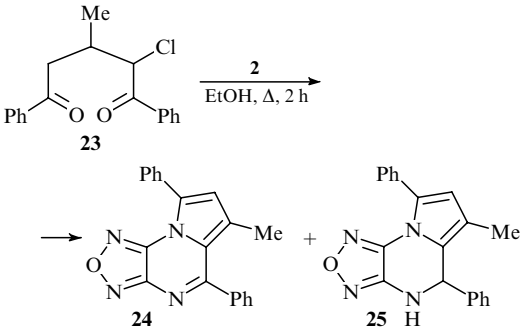
2 **19a** **19b** **19c**

Reaction of phosphoryl-substituted chloroaldehyde **20** with the diamine **2** yields hemiaminal **21**; treatment of the latter with sodium ethoxide results in cyclocondensation to give *C*-phosphorylated furazanopyrazine derivative **22**.[24]



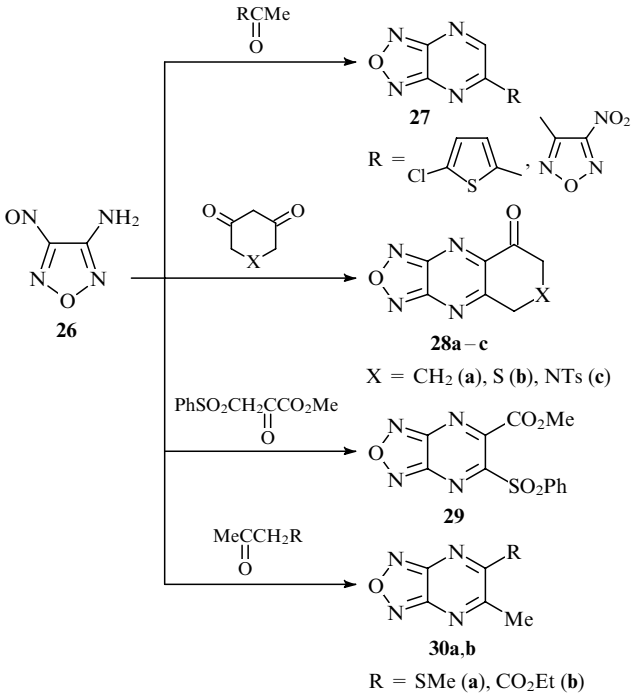
20 **21** (80%) **22** (76%)

Condensation of the amine **2** with chloro-substituted 1,5-diketone **23** gives a mixture of a tricyclic compound **24** (75%) and its dihydro derivative **25** (15%). Compound **25** is readily aromatised under the action of MnO_2; the yield of the reaction product **24** is 60%.[25]



23 **24** **25**

3-Amino-4-nitrosofurazan (**26**) is yet another furazan derivative suitable for the design of furazanopyrazines.[26] Carbonyl compounds containing a reactive methylene group, which are more accessible than α-dicarbonyl compounds, are used as the second component.[27] The one-pot reaction is carried out first in an alkaline medium (NEt_3, Na_2CO_3) which is then changed to an acidic one (AcOH). The yields of furazano[3,4-*b*]pyrazines **27**–**30** are 50%–90%. The attempts to introduce compounds with reactive methylene groups but devoid of the ketone function (*e.g*., malononitrile, ethyl cyanoacetate, nitroacetonitrile, *etc*.) into the condensation did not result in the formation of the pyrazine ring.



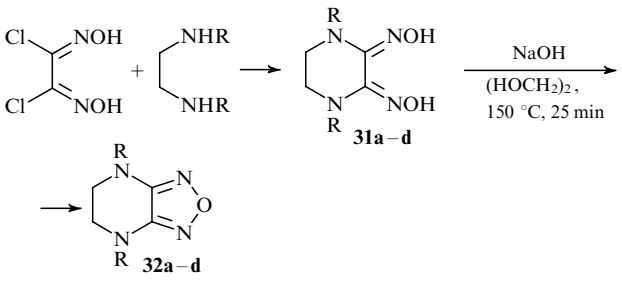
26 **27** **28a**–**c** **29** **30a**,**b**

X = CH_2 (**a**), S (**b**), NTs (**c**)

R = SMe (**a**), CO_2Et (**b**)

Furazanopyrazines can also be prepared from pyrazine precursors by fusing the furazan ring. 2,3-Bis(hydroxyimino)piperazines, which are usually prepared by reaction of dichloroglyoxime with aliphatic,[15,28,29] aromatic[30–32] or heterocyclic[33–35] 1,2-diamines, are the key compounds in this procedure.

Cyclisation of the dihydroxyimine fragment involves treatment with dehydrating agents to give the corresponding furazans or with oxidants resulting in furazan *N*-oxides (furoxans). Thus heating of an equimolar mixture of dioximes **31a**–**d** with NaOH in ethylene glycol yields the corresponding furazanopiperazines **32a**–**d**.[15,29]

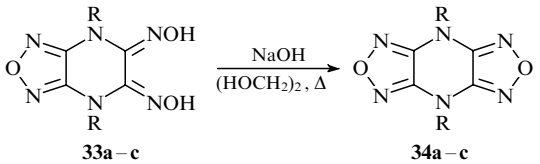


31a–**d** **32a**–**d**

R = H (**a**, 50%), Me (**b**, 52%), Pr^i (**c**, 60%), Bu^t (**d**, 75%).

Treatment of dioximes **33a**–**c** with sodium hydroxide results in closure of the second furazan ring and formation of difurazanopiperazines **34a**–**c**. Under these conditions, unsubstituted difurazanopiperazine **34a** is formed in ~ 80% yield on heating of dioxime **33a** in aqueous alkali.[35–37] Long-term treatment of the dioximes **33b**,**c** containing substituents at nitrogen atoms of the

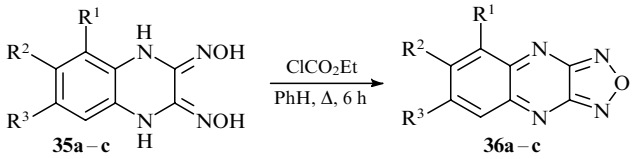
piperazine ring with sodium hydroxide in ethylene glycol yields the tricyclic products **34b**,**c**.[33,34]



33a–c **34a–c**

R = H (**a**), Bn (**b**), $CH_2C_6H_4OMe$-4 (**c**).

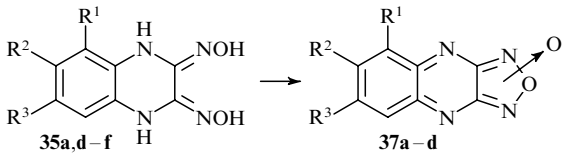
Dehydration of quinoxaline dioximes **35a–c** can be carried out by treatment with ethyl chloroformate in boiling benzene. In this case, dehydration is accompanied by aromatisation of the piperazine ring. The yields of furazanoquinoxalines **36a–c** do not exceed 50%.[38]



35a–c **36a–c**

$R^1 = R^2 = R^3 = H$ (**a**); $R^1 = R^2 = H$, $R^3 = Me$ (**b**);
$R^1 = H$, $R^1 = R^2 = Me$ (**c**).

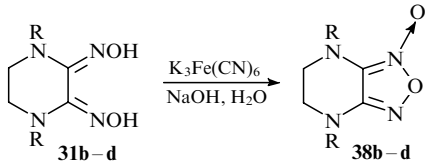
Treatment of the dioximes **35a**,**d**,**e** with bis(trifluoroacetoxy)-λ^3-iodanylbenzene results in the oxidation of both the dioxime fragment and the piperazine ring to give furoxans **37a–c**.[39] The dioxime **35f** is oxidised with lead tetraacetate, but the corresponding furoxan **37d** is formed in low yields.[31] However, the position of the *N*-oxide oxygen atom in compounds **37a–d** has not been established.[31,39]



35a,**d–f** **37a–d**

Compound **35**	R^1	R^2	R^3	Reaction conditions	Compound **37**	Yield (%)
a	H	H	H	$PhI(OCOCF_3)_2$, CH_2Cl_2, 20 °C	**a**	94
d	Me	H	H	$PhI(OCOCF_3)_2$, CH_2Cl_2, 20 °C	**b**	66
e	$(CH=CH)_2$		H	$PhI(OCOCF_3)_2$, CH_2Cl_2, 20 °C	**c**	66
f	H	Cl	H	$Pb(OAc)_4$	**d**	24

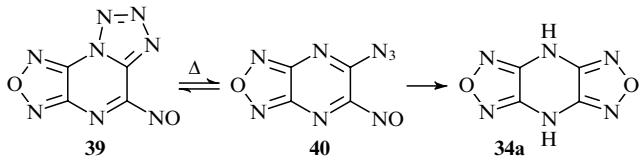
Furoxanopiperazines **38b–d** are easily prepared by oxidation of the dioximes **31b–d** with potassium ferricyanide in aqueous alkali.[15] If the starting piperazine has no substituents at nitrogen atoms (as in the case of the dioxime **31a**), no furoxan is formed.



31b–d **38b–d**

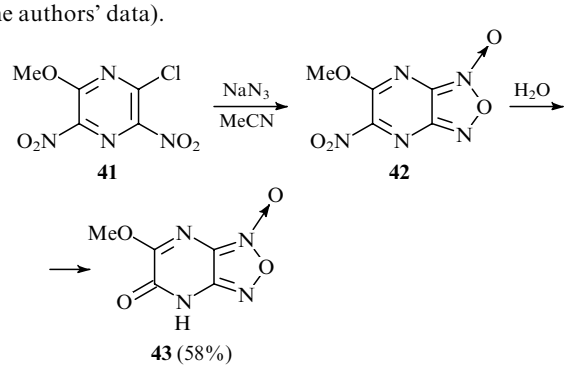
R = Me (**b**, 72%), Pr^i (**c**, 90%), Bu^t (**d**, 98%).

Thermolysis of the nitroso tetrazolopiperazine derivative **39** in AcOH–MeOH triggers a cascade of reactions which include the tetrazole ring opening, formation of the tautomer **40**, liberation of the nitrogen molecule, cyclisation of the resulting nitrene with the nitroso group and abstraction of hydrogen atoms from the solvent molecule. Difurazan **34a** is formed in 36% yield.[40]



39 **40** **34a**

Until recently, thermolysis of *o*-azidonitro compounds as a method for the synthesis of fused furoxans [4,5,41] has not been used for the preparation of furoxanopyrazines. However, it was found that gentle heating of chloropyrazine **41** with sodium azide in acetonitrile results in an immediate formation of furoxan **42**; no intermediate azide could be isolated. Furoxan **42** is unstable and is rapidly hydrolysed by the atmospheric moisture to pyrazinone **43** (the authors' data).



41 **42** **43** (58%)

The data presented suggest that the furazanopyrazine system can be formed using different approaches. The applicability of particular approach depends on the accessibility of the starting compounds and is sometimes limited by the absence of knowledge of the processes involved.

2. Chemical reactions

The data on reactions of furazanopyrazines are scarce. It is known that furazanopiperazine **32a** reacts with copper nitrate or perchlorate to give coordination compounds with the complex-forming cation linked to the nitrogen atom of the furazan rather than of the piperazine ring.[42]

Heating of furazanopyrazinone **17** in 4 M hydrochloric acid for 1 h leads to the destruction of the six-membered cycle; the reaction product, diaminofurazan **2,** is formed in 22% yield.[8]

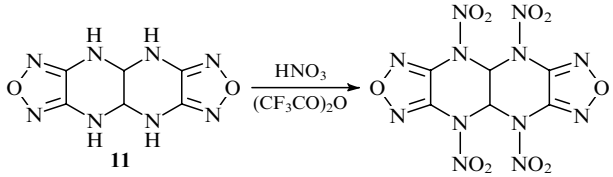
Hydrolysis of furoxanopiperazines **38b–d** is complete in 5 min upon heating in 50% ethanol. Here, the furoxan ring is opened to give the corresponding 1,4-dialkyl-2,3-dioxopiperazines.[15]

One furazan ring in difurazanopiperazine **34a** is hydrolysed to produce two carbonyl groups (Δ, HNO_3, AcOH).[35]

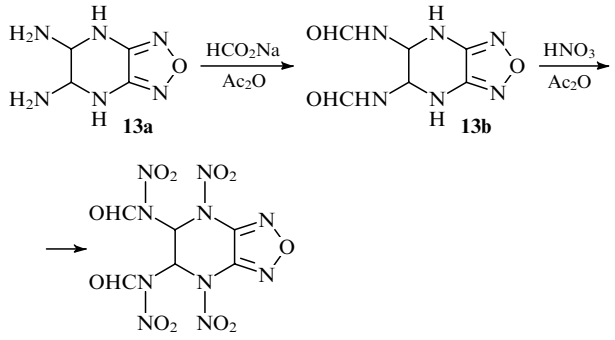
Treatment of compounds **14b**,[19] **32a** [43] and **34a** with sodium nitrite in acidic media results in their *N*-nitrosation.[35]

The overwhelming majority of published data are devoted to the synthesis and investigation of properties of nitro derivatives of furazanopyrazine. As mentioned above, some compounds of this series are promising components of explosives, propellants and gunpowders.

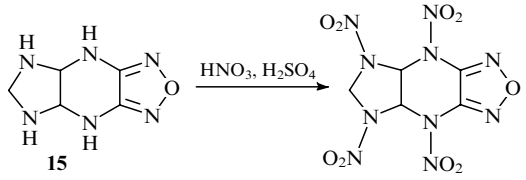
Treatment of compounds **11**,[12–15] **13b**,[16] **14a**,[16,19] **14b**,[19] **15**, **16** [16] and **32a**,**d** [15,29,37] with a mixture of 100% HNO_3 and acetic or trifluoroacetic anhydride, $HNO_3–H_2SO_4$ or $N_2O_5–HNO_3$ at low temperatures results in their nitration.

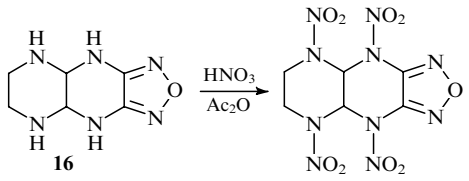


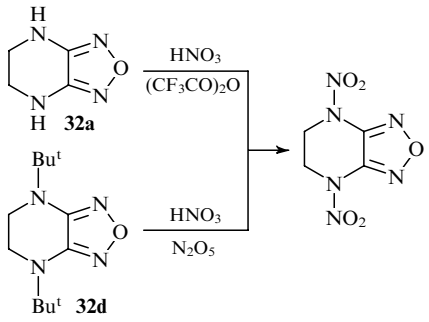
11



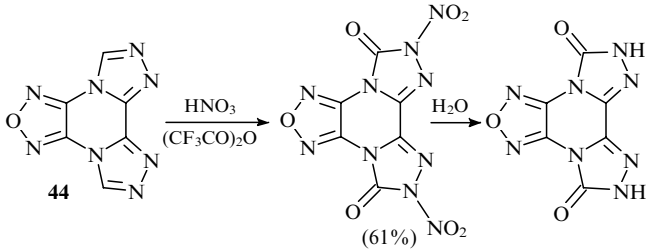
X = O (**a**), NNO_2 (**b**).



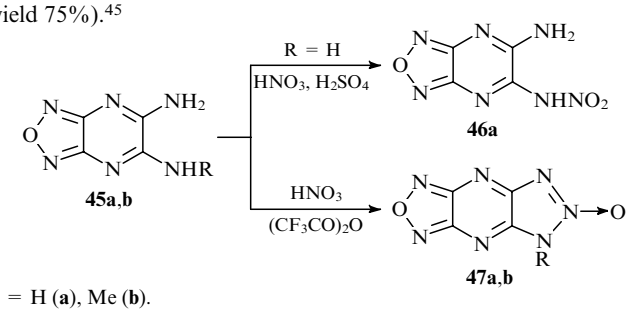




Treatment of the tetracycle **44** with an $HNO_3-(CF_3CO)_2O$ mixture results in oxidation of the C–H fragment of the triazole rings and nitration at two nitrogen atoms to give *N*-nitrotriazolone.[44] Like the aforementioned nitro compounds, this nitro derivative is easily hydrolysed.

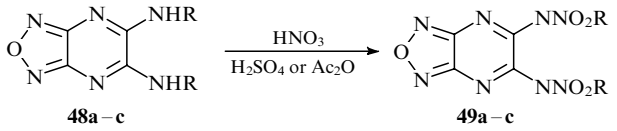


It should be noted that the diamine **13a** when treated with nitric acid forms a salt and is not nitrated.[18] At the same time, treatment of the corresponding aromatic diamine **45a** with a nitrating mixture results in its conversion into the mononitro compound **46a**. Reactions of the diamines **45a**,**b** with $HNO_3-(CF_3CO)_2O$ or BF_4NO_2 lead to the triazole ring closure and the formation of tricyclic *N*-oxides **47a** (yield 92%) and **47b** (yield 75%).[45]



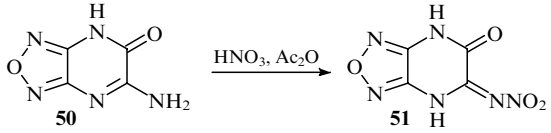
R = H (**a**), Me (**b**).

Treatment of bis(alkylamino)-substituted compounds **48a–c** with a mixture of HNO_3 and sulfuric acid or acetic anhydride gives *N*,*N*′-dinitro derivatives **49a–c**.[44,45] The yields of the reaction products do not depend on the nature of the substituent R. In the case of the hydroxymethyl derivative **48b**, the nitration affects both the nitrogen and the oxygen atoms.

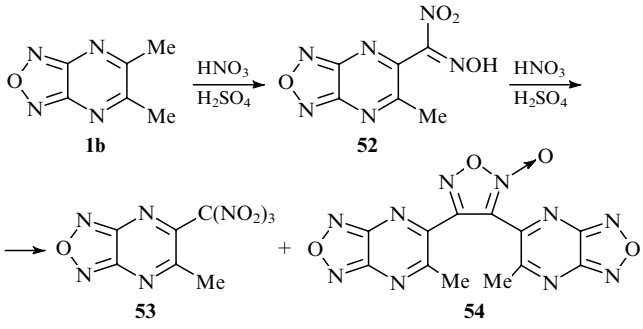


48: R = Me (**a**), CH_2OH (**b**), $CH_2C(NO_2)_3$ (**c**);
49: R = Me (**a**, 79%), CH_2ONO_2 (**b**, 82%), $CH_2C(NO_2)_3$ (**c**, 79%).

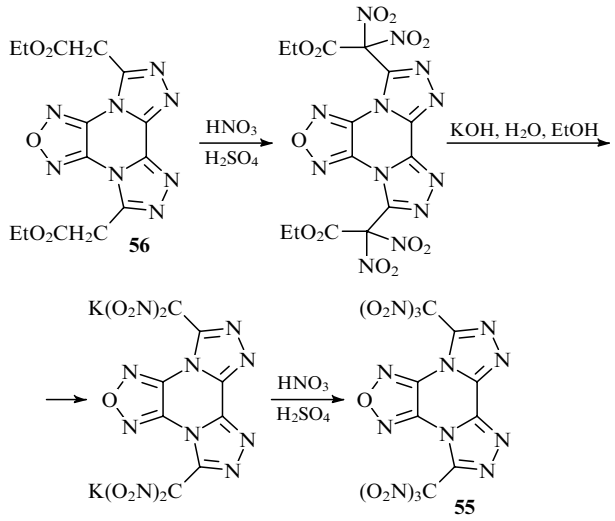
The nitration of compound **50**, containing an amino and a carbonyl group in the pyrazine ring, with an HNO_3-Ac_2O mixture gives *N*-nitroimine **51** (yield 37%). The starting compound **50** is mostly converted into dioxopiperazine **19**.[46]



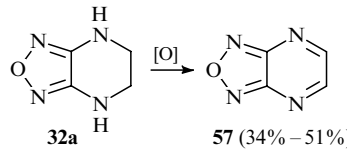
Upon treatment with an $HNO_3-H_2SO_4$ mixture, compound **1b** is nitrated and nitrosylated at the methyl group of the pyrazine ring to give nitrolic acid **52** which either undergoes further nitration with $HNO_3-H_2SO_4$ to give the trinitromethyl derivative **53** or eliminates the HNO_2 fragment to give furoxan **54**.[7] The ratio of the products **52–54** depends on the concentrations of the acids and the temperature; however, the total yields of the three compounds do not exceed 40%.[7]



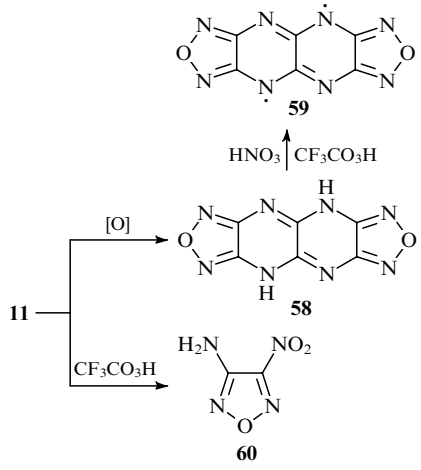
Compound **55** containing two trinitromethyl groups is prepared in three steps by stepwise introduction of nitro groups into the derivative **56**.[47]



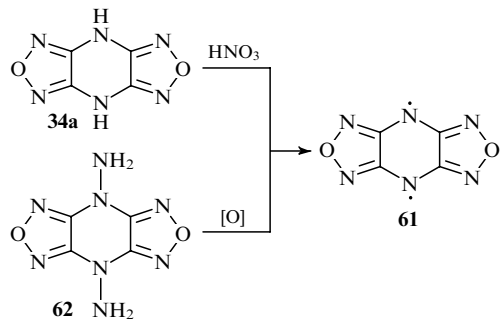
Dehydrogenation of furazanopiperazines results in their aromatisation. Thus oxidation of compound **32a** resulted in the first member of this series, *viz*., furazano[3,4-*b*]pyrazine **57**. PhIO, AgO, PbO_2 or MnO_2 are used as oxidants (the authors' data).



The oxidation of the tetracycle **11** by such oxidising agents as $K_3Fe(CN)_6$, $KMnO_4$ and $SeO_2-H_2O_2$ in water gives the dihydro derivative **58**; treatment of the latter with a nitrating mixture affords the biradical **59** in a total yield of ~ 50%. Treatment of the tetracycle **11** with trifluoroperacetic acid leads to the destruction of the six-membered cycles and the formation of furazan **60**.[48]

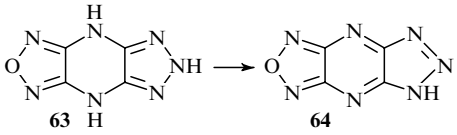


The stable biradical **61** is formed in quantitative yield by treatment of the tricycle **34a** with nitrating agents of any kind.[35,48]

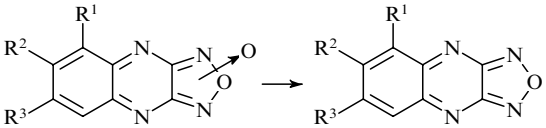


Special mention should be made of an unusual reaction of diamine **62** with oxidants which also yields the biradical **61**.[49]

Treatment of compound **63** with MnO_2 or 60% nitric acid results in the aromatisation of the piperazine ring and formation of furazanopyrazinotriazole **64**, whereas various nitrating mixtures cause the destruction of the triazole ring to the dioxo derivative **19**.[50]

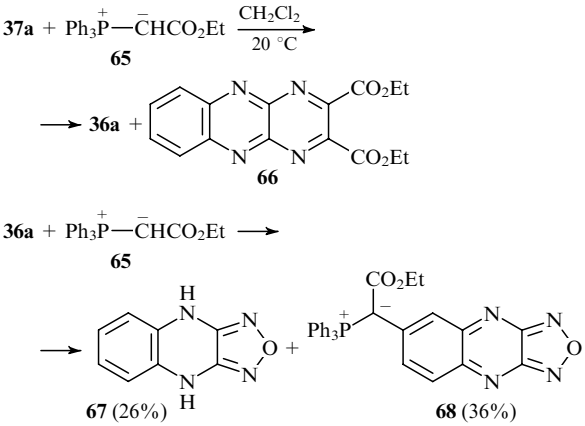


Furazanopiperazine derivatives undergo reduction. Thus furoxanoquinoxalines **37a–c** are converted into the corresponding furazans **36a,d–f** upon boiling with triethyl phosphite in ethanol.[39] Triphenylphosphine in CH_2Cl_2 causes rapid reduction of furoxan **37d** to furazan **36d**.[31] A mixture of furazans **36a** and **36d** is formed from furoxan **37a** in boiling chloroform.[31]

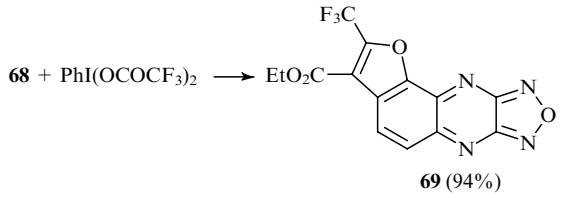


Compound **37**	Reaction conditions	Product	R^1	R^2	R^3	Yield (%)
a	$P(OEt)_3$, EtOH, 4 h	**36a**	H	H	H	35
	PCl_3, $CHCl_3$,	**36a**	H	H	H	22
	Δ, 5 h	**36d**	H	Cl	H	16
b	$P(OEt)_3$, EtOH, 4 h	**36e**	Me	H	H	35
c	$P(OEt)_3$, EtOH, 4 h	**36f**	$(CH=CH)_2$		H	50
d	PPh_3, CH_2Cl_2, 20 °C	**36d**	H	Cl	H	35

Reaction of furoxanoquinoxaline **37a** with ethoxycarbonyltriphenylphosphoniomethanide (**65**) yields a mixture of the furazan **36a** and the tricyclic derivative **66**.[51] In turn, the furazan **36a** reacts slowly with the ylide **65** to yield dihydro derivative **67** and a novel ylide **68**.[31] The formation of dihydro derivatives of the type **67** is the main reaction for furazanoquinoxalines **36d–f** containing substituents in the phenyl nucleus.[31]

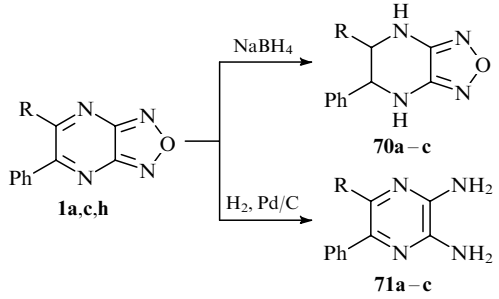


It is of note that treatment of compound **67** with bis(trifluoroacetoxy)-λ^3-iodanylbenzene results in its aromatisation and the formation of the starting furazan **36a** (yield 75%), whereas the reaction of the ylide **68** with the same reagent affords tetracyclic derivative **69** containing a fused furan ring.[31]



Electrochemical reduction of the furoxan ring in compounds **37a**,**b** has been studied.[52] The dioximes **35a**,**d** are readily formed; they can undergo more profound reduction.

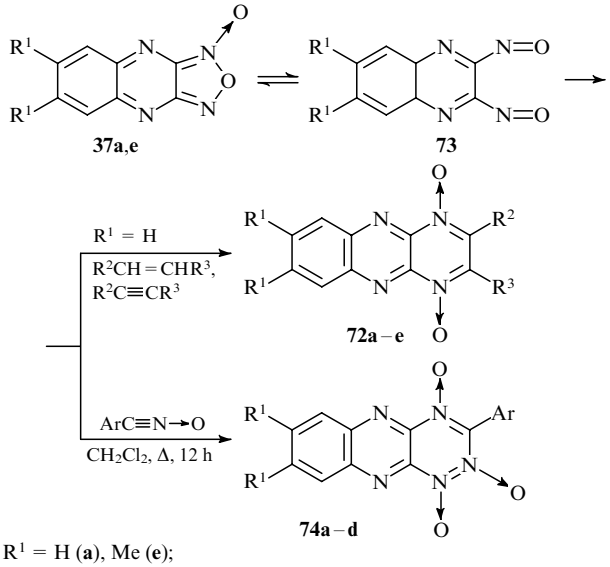
Treatment of compounds **1a**,**c**,**h** with sodium borohydride in boiling ethanol for 1 h leads to selective reduction of the pyrazine ring. The yields of piperazines **70a**–**c** are 84%–87%. Higher yields of compounds **70a**–**c** were obtained using $LiAlH_4$ as the reducing agent in boiling THF.[6] Catalytic reduction of compounds **1a**,**c**,**h** (10% Pd/C, H_2, 1 atm, ethyl acetate, 20 °C, 20 h) results in furazan ring opening and the formation of diaminopyrazines **71a**–**c** in 65%–97% yields.[6]



R = H (**1c**, **70a**, **71a**), Me (**1h**, **70b**, **71b**), Ph (**1a**, **70c**, **71c**).

Hydrogenolysis (PtO_2, H_2, ~ 50 atm, AcOH, 7 days) of N–CH_2Ph bonds in compound **34b** competes with hydrogenation of the phenyl (but not furazan) rings.[34]

Furoxanoquinoxaline **37a** reacts with alkenes and alkynes upon long-term (up to 80 h) boiling in $CHCl_3$ to yield the same

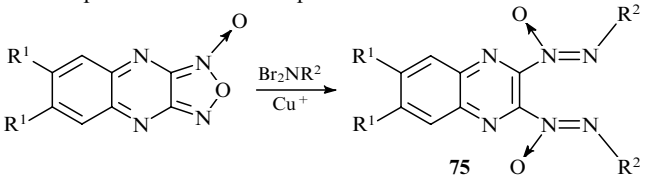


37: R^1 = H (**a**), Me (**e**);
72: R^2 = R^3 = Ph (**a**, 22–31%); R^2 = Ph, R^3 = H (**b**, 41%);
R^2 = R^3 = 4-$MeOC_6H_4$ (**c**, 47%);
R^2 = Ph, R^3 = 4-MeC_6H_4 (**d**, 19%);
R^2 = Ph, R^3 = 4-$MeOC_6H_4$ (**e**, 20%);
74: R^1 = H, Ar = 2,4,6-$Me_3C_6H_2$ (**a**, 46%);
R^1 = H, Ar = 2,6-$Cl_2C_6H_3$ (**b**, 72%);
R^1 = Me, Ar = 2,4,6-$Me_3C_6H_2$ (**c**, 54%);
R^1 = Me, Ar = 2,6-$Cl_2C_6H_3$ (**d**, 63%).

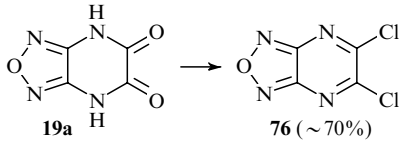
products, *viz*., di-*N*,*N*′-oxides **72a**–**e**.[53] This transformation proceeds in accordance with the so-called Beirut reaction [41] where the *o*-dinitroso compound **73**, a valent tautomer of furoxan, plays the role of an intermediate.

Unusual tri-*N*,*N*′,*N*″-oxides **74a**–**d** were prepared by reaction of furoxans **37a**,**e** with arenecarbonitrile oxides. This reaction also involves the dinitroso intermediate **73**. A feasible mechanism of the formation of compounds **74a**–**d** has been proposed.[54]

Presumably, the formation of bis(azoxy)quinoxalines **75** (yields ~ 50%) in the reaction of furoxans with *N*,*N*-dibromoamines catalysed by Cu(I) ions proceeds *via* the corresponding dinitroso intermediates.[55] Unfortunately, no details of the experimental protocol have been reported.

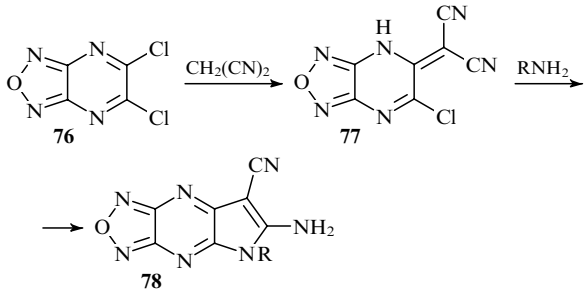


Of special interest is the use of the dichloro derivative **76** in the synthesis of various furazano[3,4-*b*]pyrazines. Compound **76** is prepared on heating of the diketone **19a** with thionyl chloride,[47,56] $POCl_3$ in the presence of a catalytic amount of DMF or a $POCl_3$–PCl_5 mixture.[56]



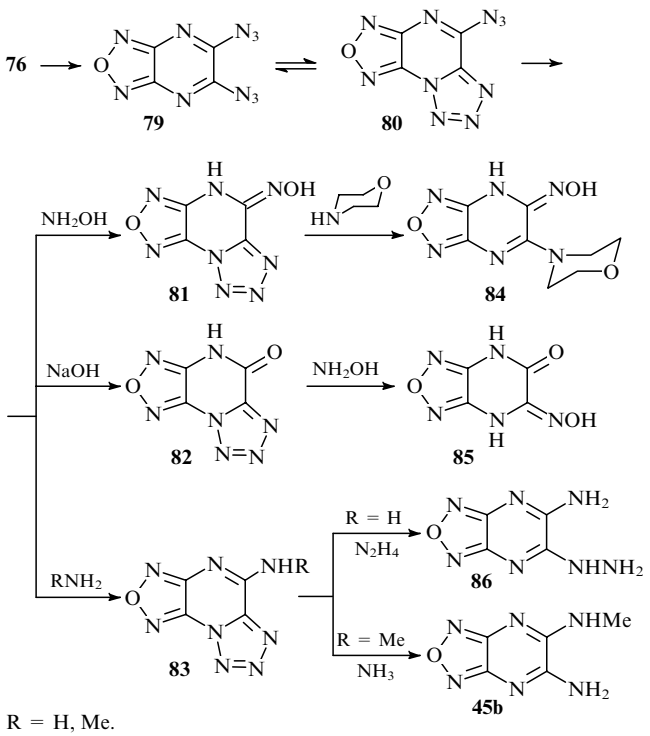
Since the furazano[3,4-*b*]pyrazine system is a typical π-acceptor, the halogen atoms in compound **76** manifest high activity towards nucleophiles. The reactivity of the dichloride **76** exceeds markedly those of its analogues containing 1,2,5-thiadiazole and triazole rings instead of the furazan ring as well as 2,3-dichloroquinoxaline and tetrachloropyrazine.[56]

Thus reactions of dichloride **76** with ammonia, alkyl- and arylamines,[56] hydroxylamines,[35,36,56] hydrazines,[47,56] azide ion,[57] alcohols,[56,58] phenols,[56] hydroxyfurazans [58] and thiols [56,59] proceed smoothly with substitution of both chlorine atoms. The corresponding products are formed in high yields. Selective substitution of only one chlorine atom can sometimes be achieved by varying reaction conditions [40,56] and using weak or sterically hindered nucleophiles.[56,60–62] The second chlorine atom in the monosubstitution products can be replaced by another nucleophile.[40,56,60,61] Thus the one-pot reaction of the dichloride **76** with the malonodinitrile anion yields dicyanomethylidene derivative **77** which cyclises into tricyclic aminonitriles **78** upon treatment with amines.[60,61] The yields of compounds **78** are 90%–95%.



R = Alk, Ar, Het *etc*.

An original procedure for the synthesis of non-symmetrical furazanopyrazine derivatives involves the substitution of the azido groups for the chlorine atoms in compound **76** and subsequent reaction of the azido derivative **79** with nucleophiles.[57,63]

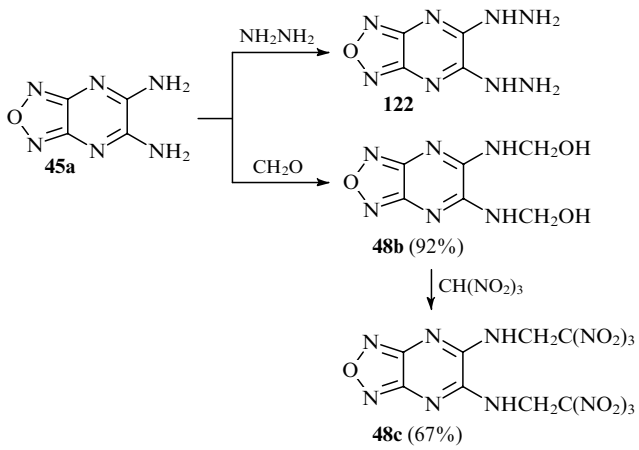


R = H, Me.

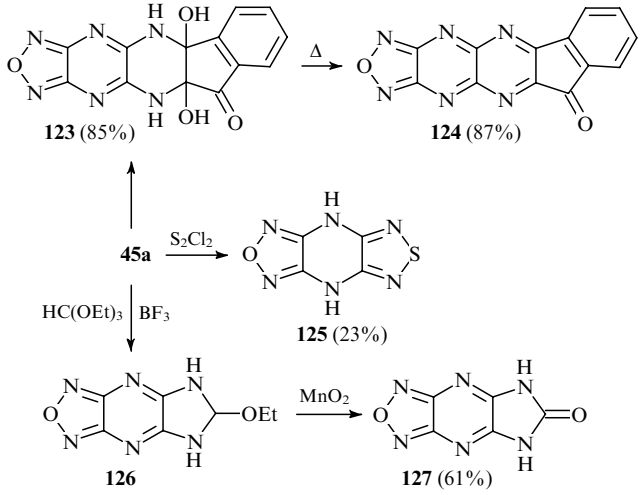
Owing to azido–tetrazole tautomerism, one of the azido groups in compound **79** exists in a cyclic form. This stabilises the remaining azido group of the tautomer **80** and makes it less mobile than the chlorine atoms in the dichloride **76**. Replacement of one azido group is complete in ~ 1.5 h at 20 °C. Incubation of the reaction mixture for ~ 24 h results in replacement of the second azido group. The yields of monosubstitution products, such as compounds **81**–**83,** are 76%–85%.[57,63] Subsequent long-term (~ 24 h) treatment with another nucleophile yields non-symmetrical compounds **45b**, **84**–**86**, which can be difficult to synthesise by other methods.

High reactivities of both the chlorine atoms in compound **76** were employed in the synthesis of polycyclic heterocycles incorporating a furazanopyrazine fragment. Thus reactions of the dichloride **76** with 1,3- and 1,4-dinucleophiles, such as diamines, amino and mercapto alcohols, aminothiols, thiourea, 2-aminoazoles, 2-aminoazines and *N*-benzoylglycine in acetonitrile at 20 °C yield polycyclic compounds **87**–**121** (Table 2). In the majority of cases, these reactions occur in the absence of a base (method A). However, the use of weakly nucleophilic reagents requires addition of triethylamine or other analogous bases (method B). The yields of reaction products depend on the nucleophilicities and steric characteristics of the starting reagents.

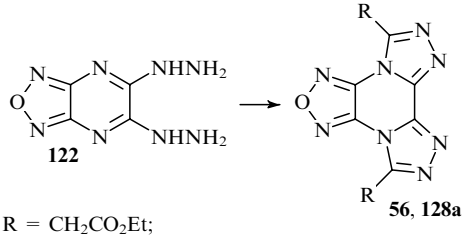
The amino groups of the diamine **45a**, which is readily prepared from the dichloride **76**,[56] are deactivated owing to the electron-withdrawing effect of the fused ring system. Attempts at alkylation of the amine **45a** with alkyl and aryl halides, halogeno ketones, diethyl carbonate and dichloroglyoxime were unsuccessful. This amine does not form stable salts even with strong acids.[44] Its treatment with oxidising mixtures based on H_2O_2 causes its degradation. At the same time, the electron-withdrawing nature of the ring allows replacement of the amino groups upon treatment with hydrazine to give bishydrazine **122**. Treatment of the diamine **45a** with formaldehyde yields the bis(hydroxymethyl) derivative **48b** which is stable owing to the electron-withdrawing character of the bicyclic fragment. Treatment of compound **48b** with trinitromethane gives the Mannich base **48c**.[44] Analogous Mannich bases were prepared from cyclic compounds containing NH groups.[46]



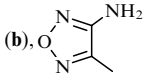
A series of fused furazanopyrazine derivatives were synthesised from the diamine **45a.** Its reaction with ninhydrin in AcOH results in the dihydroxy derivative **123**.[11] Heating of compound **123** in ethanol, DMF or H_2SO_4 for more than 3 h is accompanied by dehydration and formation of a pentacyclic product **124**. Thiadiazole **125** was prepared by treating the amine **45a** with sulfur monochloride.[44] Condensation of the amine **45a** with triethyl orthoformate in the presence of a Lewis acid gives tricyclic compound **126** which is converted into imidazolone **127** on oxidation with MnO_2.[44]



Treatment of the bishydrazine **122** with HNO_2 gives the tetrazole **80**,[57] while its heating with acids, acid anhydrides[44] or imidates[47] results in simultaneous formation of two triazole rings. The tetracyclic derivatives **56** and **128a**–**c** are formed in 60%–90% yields. The methyl groups in compound **128b** were oxidised to carboxy groups with potassium permanganate.[44]



56: R = CH_2CO_2Et;

128: R = H (**a**), Me (**b**),  (**c**).

An unusual polycyclic system **129** was obtained upon oxidation of amine **130** with subsequent thermolysis of azo derivative **131**.[63] However, the total yield of compound **129** did not exceed 20%.

Table 2. The reaction of 5,6-dichlorofurazano[3,4-*b*]pyrazine with dinucleophiles.

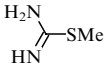
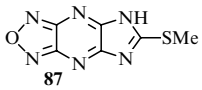
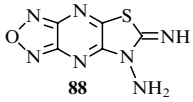
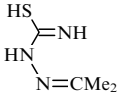
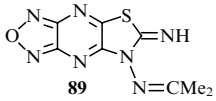
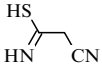
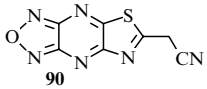
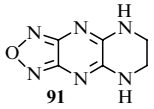
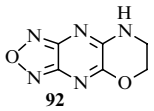
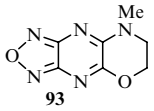
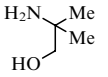
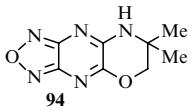
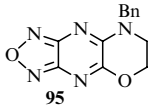
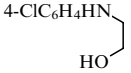
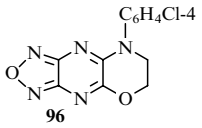
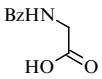
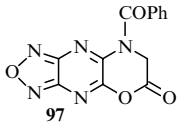
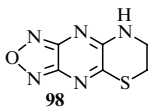
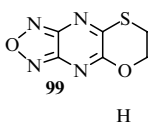
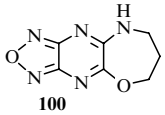
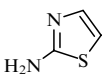
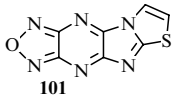
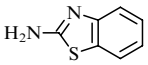
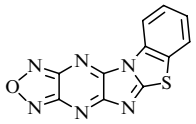
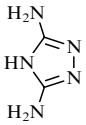
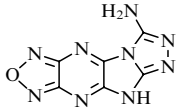
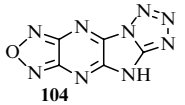
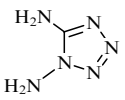
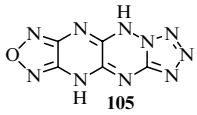
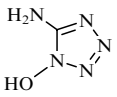
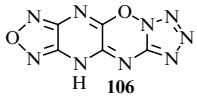
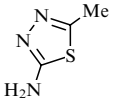
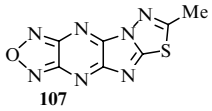
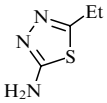
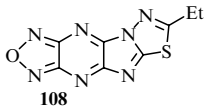
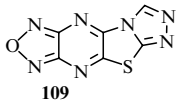
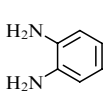
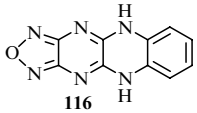
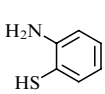
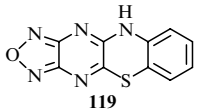
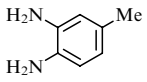
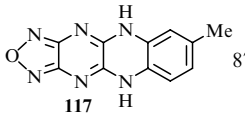
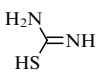
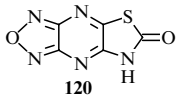
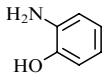
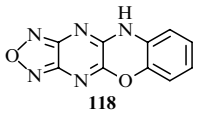
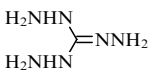
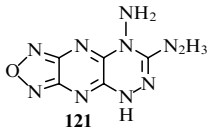
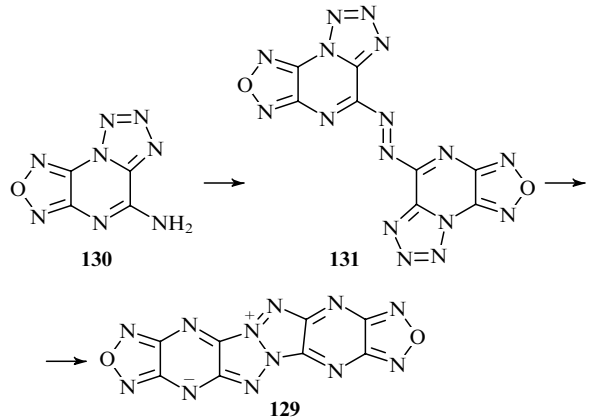
Dinucleophile	Reaction conditions	Structure	Yield (%)	Ref.
	A	 **87**	58	64
	B	 **88**	62	64
	A	 **89**	73	64
	B	 **90**	64	60
$H_2N(CH_2)_2NH_2$	B	 **91**	46	64
$H_2N(CH_2)_2OH$	A	 **92**	72	64
$MeHN(CH_2)_2OH$	B	 **93**	83	64
	A	 **94**	32	64
$BnHN(CH_2)_2OH$	B	 **95**	48	64
	A	 **96**	92	64
	A	 **97**	18	64
$H_2N(CH_2)_2SH$	A	 **98**	80	64
$HS(CH_2)_2OH$	A	 **99**	75	64
$H_2N(CH_2)_3OH$	A	 **100**	47	64
	A	 **101**	42	64
	A B	 **102**	58 89	see [a]
	A	 **103**	66	64
	A	 **104**	36	64
	B	 **105**	28	63
	B	 **106**	24	63
	A	 **107**	62	64
	A	 **108**	58	64
	A	 **109**	55	64
	B	**110**	81	64
	A B	**111**	41 77	see [a]
	A B	**112**	12 35	see [a]
	B	**113**	23	see [a]
	A B	**114**	18 67	see [a]
	B	**115**	18	see [a]

Table 2 (continued).

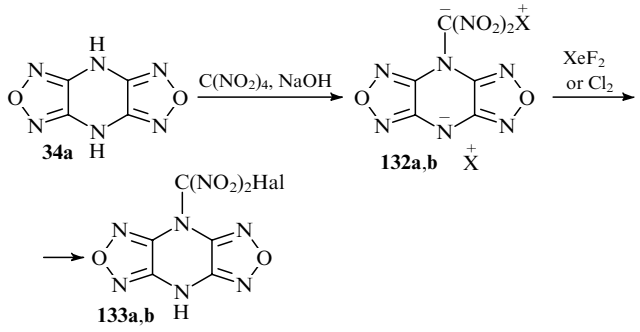
Dinucleophile	Reaction conditions	Structure	Yield (%)	Ref.	Dinucleophile	Reaction conditions	Structure	Yield (%)	Ref.
	B	 **116**	93	64		A	 **119**	81	64
	A	 **117**	87	64		B	 **120**	28	64
	A	 **118**	72	64		A	 **121**	43	63

Note. A, in the absence of a base; B, in the presence of a base. [a] The authors' data.



130 **131** **129**

Polycyclic compounds containing NH groups represent acids of moderate strength. For example, pK_a^1 for the difurazanopiperazine **34a** is 6.96, whereas pK_a^2 is 10.17.[35,48] It is acylated [35,48] or alkylated (arylated) [35,48,50] under ordinary conditions. Compound **34a** reacts specifically with tetranitromethane in an alkaline medium to give disodium salt of dinitromethyl derivative **132** in 75% yield.[35] Trinitromethyl reagents react in a similar way.

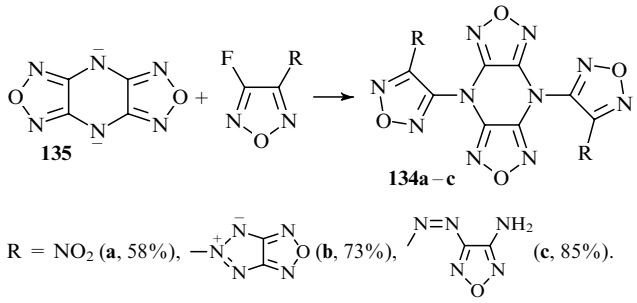


34a **132a,b** **133a,b**

X^+ = Na (**132a**), K (**132b**); Hal = F (**133a**, 78%), Cl (**133b**, 90%).

Reaction of the disodium salt **132a** with XeF_2 or Cl_2 gives the corresponding halogen derivatives **133a,b**.[35] Compound **133a** is also formed upon treatment of the dipotassium salt **132b** with XeF_2.[47]

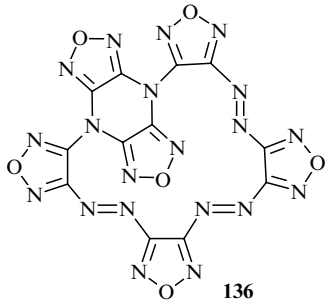
Compounds **134a–c** containing two furazanylamine fragments were prepared by a reaction of a dianion **135** with the corresponding fluorofurazans.[65,66] By varying the reaction conditions, one can direct the reaction to the predominant formation of the monoaddition product.



135 **134a–c**

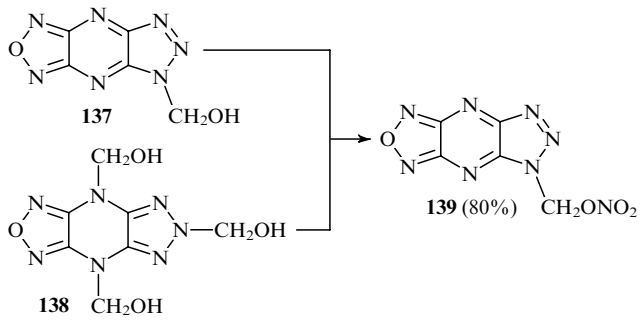
R = NO_2 (**a**, 58%), (**b**, 73%), (**c**, 85%).

Oxidation of the diamine **134c** with dibromoisocyanurate results in intramolecular crosslinking of the amino groups into an azo group to yield macrocycle **136**.[65,66]



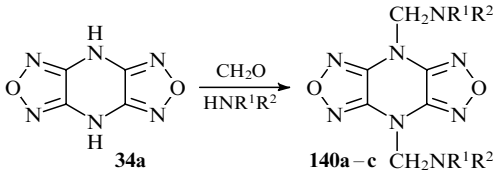
136

Reactions of polycyclic compounds containing NH groups with formalin give *N*-hydroxymethyl derivatives; treatment of the latter with HNO_3-Ac_2O or $HNO_3-(CF_3CO)_2O$ results in their conversion into the corresponding nitroxymethyl derivatives.[44,48,50] It should be noted, however, that both mono- (**137**) and tris(hydroxymethyl) derivatives (**138**) yield the same nitrate **139**.[50]



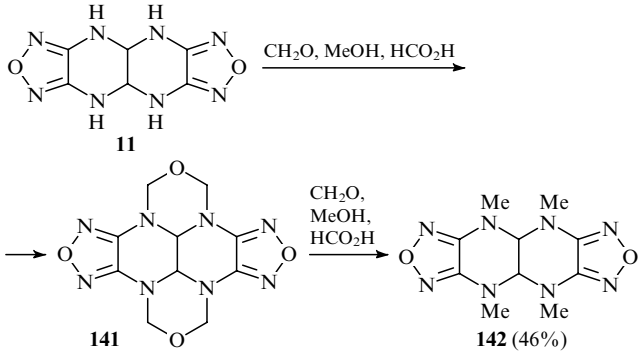
137 **138** **139** (80%)

N-Hydroxymethyl derivatives are acylated with acetic anhydride; their treatment with $SOCl_2$ yields chloromethyl derivatives. The chlorine atom in the latter can be substituted for the azido group under the action of sodium azide.[48] Mannich bases **140a–c** were obtained in nearly quantitative yields using a three-component reaction of the difurazanopiperazine **34a** with CH_2O and amines.[48]

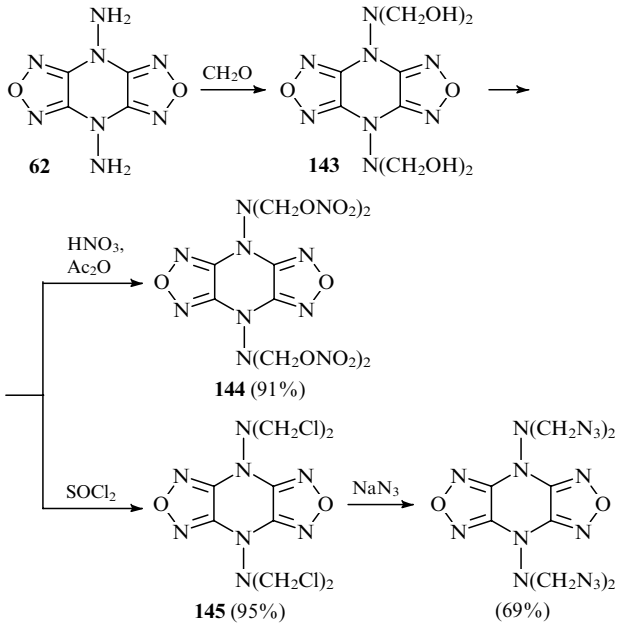


R^1R^2N = $NH(CH_2)_2SH$ (**a**), NHC_6H_4Cl-4 (**b**),  (**c**).

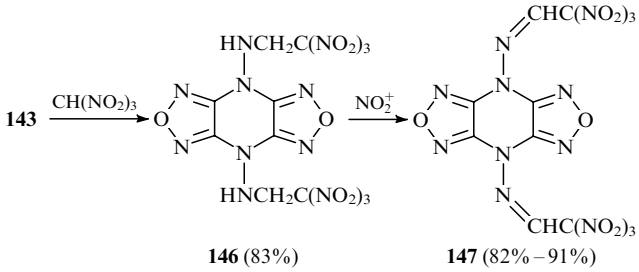
Short-term heating of the tetracyclic compound **11** with formaldehyde in a methanol–formic acid mixture results in the polycycle **141** in quantitative yield. Boiling of the reaction mixture for 36 h results in partial reduction of compound **141** to the tetramethyl derivative **142**.[67]



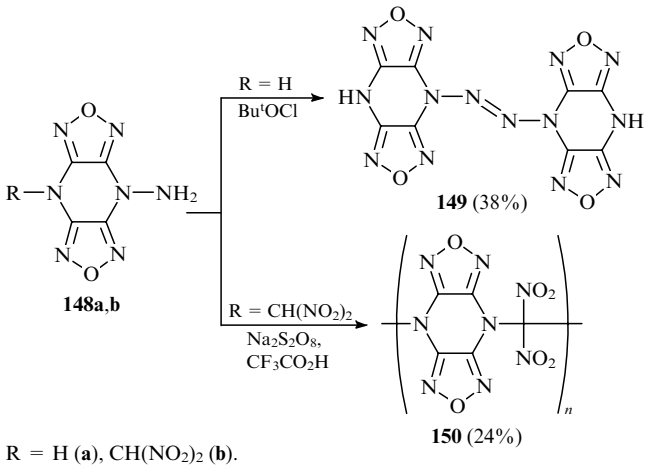
Polycyclic compounds containing NH groups are aminated upon treatment with hydroxylaminosulfonic acid to give *N*-amino derivatives.[48,49,63] *N*,*N*′-Diaminopiperazine **62** reacts with aldehydes to yield bishydrazones; its acylation gives a *N*,*N*,*N*′,*N*′-tetraacetyl derivative.[48] The conversions of bis(bishydroxymethylamino)piperazine **143** prepared in the reaction of the diamine **62** with formaldehyde have been studied.[48]



Thus nitration of compound **143** with an $HNO_3–Ac_2O$ mixture gave nitrate **144**. Reaction with thionyl chloride yields tetrachloride **145**, the chlorine atoms in which are reactive enough to be substituted by the azide ion.[48] Reaction of the hydroxymethyl derivative **143** with nitroform results in splitting of two hydroxymethyl groups to give bis(trinitroethylamino)piperazine **146**, which affords trinitroacetaldehyde **147** instead of nitramine upon nitration with various nitrating reagents.[48,63]



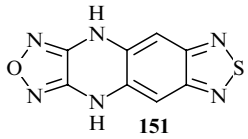
In contrast to oxidation of the diamine **62**, which generates the biradical **61**, treatment of monoaminopiperazine **148a** with *tert*-butyl hypochlorite affords an unstable tetrazene **149**.[49] A similar monoamine **148b** undergoes oxidation by sodium persulfate in trifluoroacetic acid to the oligomer **150**.[49]



R = H (**a**), $CH(NO_2)_2$ (**b**).

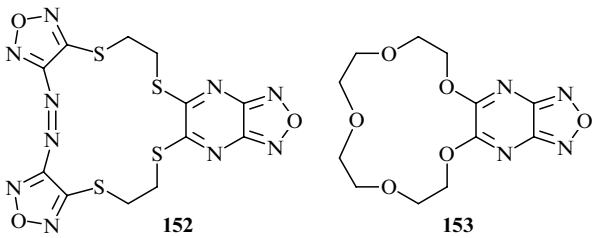
3. Properties and applications

The biological activities of furazano[3,4-*b*]piperazines have been little studied. Compound **1c** has been patented as a herbicide.[9] The oxo derivatives **18a–d** have been recommended as tranquilizers.[23] Furazanopiperazine **151** and its derivatives were found to possess biocidal activities.[68]



The macrocyclic compound **136** was used as an inhibitor of the soluble form of guanylate cyclase.[65]

The sulfur-containing macrocycle **152** was regarded as a candidate complexone,[59] but compound **153** proved to be more efficient. The latter forms adducts with alkali metal nitrates and perchlorates as well as with dinitramine salts (the authors' data).

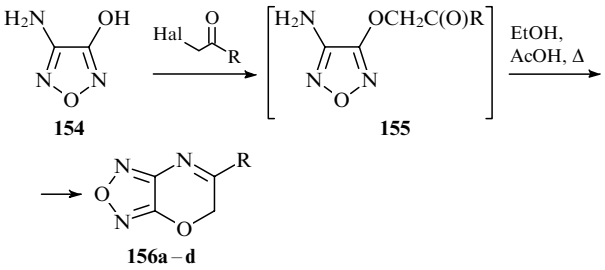


Furazanopiperazine **32a** possesses interesting photoelectric properties which are manifested as specific effects during electron movements in thin layers.[69–71]

However, nitro and other polynitrogenous furazanopyrazane derivatives attract the most attention. Various thermochemical and explosive properties of their derivatives have been studied. Although most of these data are known to specialists only, some evidence can be found in popular literature. Characteristics of some compounds, *viz*., detonation rate;[12,13,16,29,37] shock, friction and flame sensitivity;[12,14,16,29] enthalpy;[14,29,27,72] thermal stability and thermal degradation [16,63,72–78] and combustion,[46,63] have been established and documented. Such parameters as density,[12,13,29,33,37,46,79] enthalpy,[37,46,79,80] detonation rate,[12,13,29,33,79] detonation pressure,[12–14,29,33] temperature and other combustion characteristics have been studied using computer methods.[46,63] The possibility of using nitro derivatives as components of explosive and pyrotechnical compositions and propellants has been considered.[12–14,16,29,37,46,63,80,81]

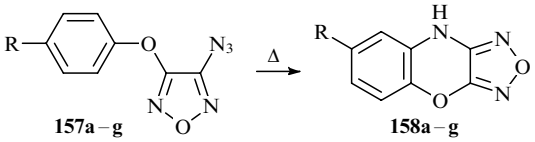
III. Furazano[3,4-*b*][1,4]oxazine derivatives

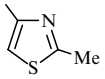
Both methods presently employed in the synthesis of furazanoxazine derivatives are based on the use of compounds of the furazan series. Thus 3-amino-4-hydroxyfurazan **154** reacts with α-halogeno ketones in the presence of NEt_3 to give the intermediates **155** which undergo *in situ* cyclisation upon heating in an ethanol–AcOH mixture to give bicyclic derivatives **156a–d**.[2]



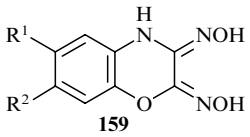
R = Me (**a**), CH_2Cl (**b**), Ph (**c**),  (**d**).

Thermolysis of 4-aryloxy-3-azido-furazans **157a–g** in decalin was used to obtain tricyclic compounds **158a–g** (the authors' data). It is of note that cyclisation occurs smoothly only with the *para*-substituted derivatives **157a–g**; reaction products are formed in 43%–72% yields. Attempts to use compounds with an *ortho*- or *meta*-substituent in the phenyl ring resulted in a complex mixture of products. The possibilities of this method are also limited by accessibility of the starting azides **157a–g**.



R = Cl (**a**), F (**b**), NMe_2 (**c**), Me (**d**), OMe (**e**), Ph (**f**),  (**g**).

The structural similarity of phenoxazine derivatives endowed with physiological activities and compounds of the type **158** makes them attractive targets for synthesis. However, attempts to fuse the furazan ring to the benzoxazine ring by treatment of dioximes **159** with ethyl chloroformate (which has been employed in the synthesis of the furazanoquinoxalines **36a–c**) were unsuccessful.[38]

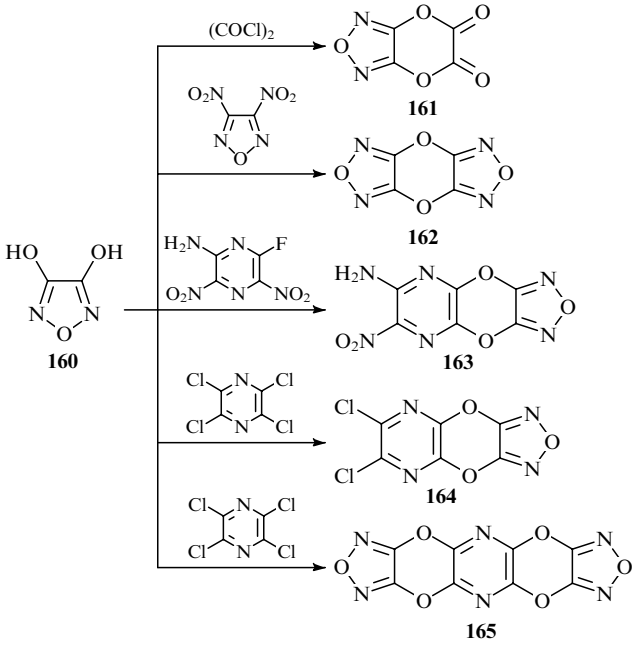


R^1, R^2 = H, Me, Cl.

There is still no information on the reactivities of furazanoxazine derivatives in the literature.

IV. 1,4-Dioxino[2,3-*c*]furazan derivatives

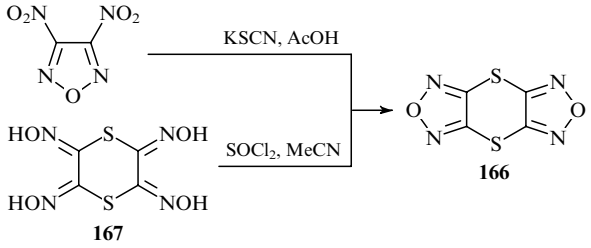
Only one method for the construction of 1,4-dioxino[2,3-*c*]furazan derivatives is known. The key building block is 3,4-dihydroxyfurazan **160**.[58,82] Its treatment with oxalyl chloride in the presence of triethylamine in CH_2Cl_2 gives dioxo derivative **161**.[63] Reaction of compound **160** with 3,4-dinitrofurazan affords a mixture of products from which the tricyclic derivative **162** was isolated in 12% yield.[83]



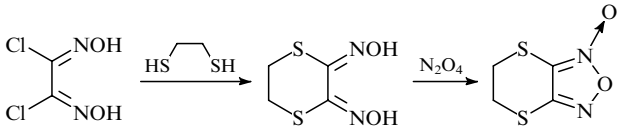
Compounds **163–165** were synthesised by the reaction of salts prepared from compound **160** with the corresponding halogeno pyrazines under conditions of phase-transfer catalysis.[58,84–86] The pyrazine ring in compound **163** was oxidised to di-*N*,*N*′-oxide upon treatment with peroxy acids.[84]

V. 1,4-Dithiino[2,3-*c*]furazan derivatives

1,4-Dithiino[2,3-*c*]furazan derivatives were prepared starting from compounds of both the furazan and dithiine series. Both approaches were used for the synthesis of dithiinodifurazan **166**. This is the reaction product of 3,4-dinitrofurazan with potassium thiocyanate (yield 27%).[87] Dehydration of tetroxime **167** with thionyl chloride also yields compound **166**.[88]



Oxidation of dioxime **168** (prepared from dichloroglyoxime and 1,2-ethanedithiol) with nitrogen oxides affords furoxan derivative **169**, which is recommended as a cardiostimulator along with acyclic thio-substituted furoxans.[89]



168 **169** (71%)

No other data on the possible applications and reactivities of heterocyclic derivatives are available.

* * *

The data presented suggest that the most impressive success has been achieved in the chemistry of furazanopyrazine derivatives, whereas furazans fused to other six-membered heterocycles with two heteroatoms in positions 1 and 4 have been little explored. Further efforts in this branch of chemistry will be aimed at the search for useful properties of furazan fused to pyrazines, oxazines, dioxines and dithiines which, in turn, will stimulate the development of convenient methods for their synthesis. We hope that this review will be helpful for both chemists and specialists in other fields.

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