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The chemistry of furazans fused to six- and seven-membered heterocycles with one heteroatom

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Abstract. The data on the synthesis and properties of furazan derivatives fused with pyridine, pyran, thiopyran, azepine and thiepine rings are surveyed and described systematically. The bibliography includes 85 references.

I. Introduction

Furazan (1,2,5-oxadiazole) derivatives are heterocyclic compounds of a non-natural origin. The first representatives of furazans were synthesised more than a hundred years ago. The subsequent development of the chemistry of this class of compound has been stimulated both by the diversity of their chemical transformations and by a number of their interesting properties, which provide the possibility of using them in medicine, agriculture and some fields of engineering.

In this decade alone, the peculiar behaviour of furazans and their *N*-oxides (furoxans) and the large body of information, which permanently extends as a result of studies of numerous groups of researchers, have led to the publication of several reviews [1–10] and monographs.[11, 12]

Fused systems consisting of two or more heterocycles, of which at least one heterocycle is a furazan ring, deserve close attention both from the theoretical viewpoint and due to the possible application of these compounds as intermediates in synthesis. Some derivatives of this class have been proposed as herbicides, rubber modifiers, liquid crystals, luminescent dyes and explosives.

Systems in which a furazan ring is fused to a five-membered heterocycle have been considered in a review.[6] The present review is devoted to the least studied derivatives, furazans fused to six- and seven-membered heterocycles with one heteroatom.

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II. Furazan ring as a fragment of a bicyclic system

Furazan can be regarded as a hetero-analogue of cyclopentadiene. On passing from electron-releasing cyclopentadiene to electron-withdrawing furazan, chemical properties are virtually reversed. One can say that furazan is a sort of antipode of cyclopentadiene.

Successive replacement of carbon atoms by heteroatoms results in redistribution of electron density and in enhancement of π-acceptor properties of the system in the following series: cyclopentadiene, furan, isoxazole, furazan.

In all of these rings, electronic effects of substituents are transferred solely through the (hetero)diene system of bonds.[13] The CH_2 group (in cyclopentadiene) and oxygen atoms (in the other three rings) act as a sort of insulator for this transfer. As a consequence, the degrees of aromaticity of these four cyclic systems are approximately equal.

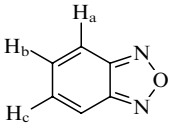
Compound				
Aromaticity index (*I*)[14]	45	43	47	43

It should be noted that the degree of bond order fixation in the heterodiene system of furazan is extremely high; derivatives of this heterocycles are not susceptible to annular-group tautomerism.

The chain consisting of three heteroatoms, present in the furazan molecule, accounts for the substantial electron-withdrawing properties of this heterocycle.[15–17] The Taft induction constants σ* of 4-R-furazanyl groups (as substituents) fall in the range 2.55 – 2.88 (these values correspond to R = NH_2 and R = NO_2, respectively).[18] For comparison, the σ* value of the 3-furyl group is 0.62. The well-known electron-withdrawing picryl group, 2,4,6-$(NO_2)_3C_6H_2$ has a σ* value of only 1.62. The following substituents are characterised by σ* constants close to that of furazan: CH = $C(CN)_2$ (σ* = 2.56), CF_3 (σ* = 2.6); $CBr(NO_2)_2$ (σ* = 2.8); 5-tetrazolyl group (σ* = 2.82); nitrile group (σ* = 3.25).[19]

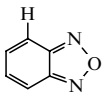
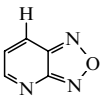
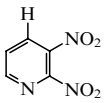
The reactivity of annelated furazan derivatives is also significantly affected by the nature of the second ring — its size, the number of heteroatoms and their type and positions. A typical feature of annelated furazans is bond order fixation over the whole contour of the bicyclic system. It is known that the degree of delocalisation of π electrons in benzoannelated heterocycles can be estimated using the Gunther method[20] based on the ratio of spin-spin coupling constants, J_{bc}/J_{ab}. When the bonds are fully

equivalent, as in benzene, this ratio is equal to unity, whereas completely localised bonds correspond to a ratio of 0.5. According to ^{1}H NMR spectroscopy, the J_{bc}/J_{ab} ratio for benzofurazan is 0.706; in other words the bonds are substantially localised.[21]

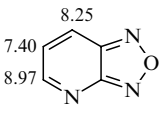


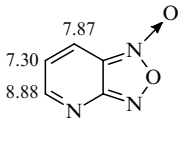
The replacement of one =CH– unit in the benzene molecule by an isoelectronic fragment, =N–, is known to result in a less uniform distribution of electron density and more pronounced localisation.[14] In fact, on passing from benzofurazan to furazano[3,4-*b*]pyridine, the spin-spin coupling constant for protons a, b changes only slightly (J = 9.34 Hz for benzofurazan[22] and J = 9.00 Hz for furazanopyridine[23]), whereas the constant for protons b, c changes more significantly (J = 6.50 and 3.70 Hz, respectively). Evidently, this points to a decrease in the order of the b–c bond and, hence, to an increase in the degree of localisation upon the replacement of the =CH– fragment by =N–.

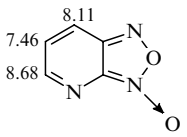
On passing from benzene to pyridine and then from benzofurazan[22] to furazanopyridine,[23] the ^{1}H NMR signal shifts downfield, which is also due to a decrease in the electron density in this series. However, it should be mentioned that the influence of the furazan ring is still weaker than that of two *ortho*-nitro groups.

Compound					
					
δ, ppm	7.27	7.46	7.96	8.25	8.92

The *N*-oxide fragment acts as a resonance electron-releasing group of medium strength;[14] therefore, on passing to the *N*-oxide, furoxanopyridine, the electron-withdrawing influence of the furazan ring becomes weaker. In particular, the signals of the protons at C(7) in the ^{1}H NMR spectra of both isomers of furoxanopyridine are shifted upfield in relation to corresponding signal in the spectrum of furazanopyridine.[23]



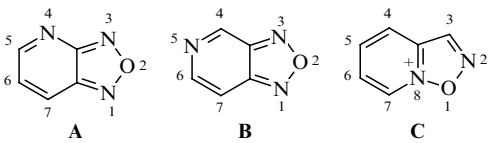




Theoretical calculations[24] and polarographic studies[25–29] have also been used to describe the influence of the furazan ring on the properties of molecules incorporating it. Acid–base properties of some annelated furazan derivatives have also been studied.[30]

III. Furazanopyridines

Derivatives of all three possible types of bicyclic systems based on furazan and pyridine rings — furazano[3,4-*b*]pyridine (**A**), furazano[3,4-*c*]pyridine (**B**) and furazano[3,4-*a*]pyridine (**C**) — have been described in the literature.

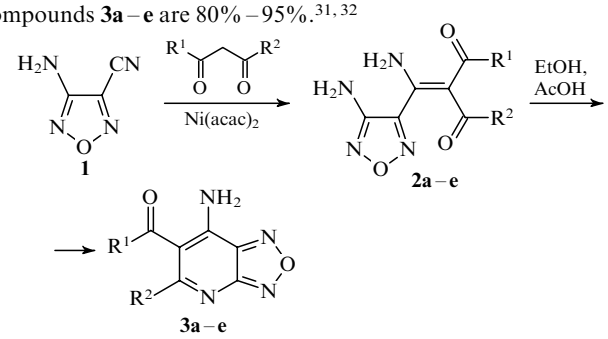


A **B** **C**

1. Furazano[3,4-*b*]pyridine

The heterocyclic system of furazano[3,4-*b*]pyridine (**A**) is also referred to as 1,2,5-oxadiazolo[3,4-*b*]pyridine and the corresponding 1(3)-oxides are also called furoxano[3,4-*b*]pyridines and pyridofuroxans.

Derivatives of the bicyclic system **A** can be obtained from both furazan and pyridine synthons. Thus the reaction of 3-aminofurazan-4-carbonitrile **1** with β-dicarbonyl compounds in the presence of a catalytic amount of nickel acetylacetonate gives rise to labile enamines **2a–e**. On heating with acetic acid in ethanol, they undergo intramolecular condensation to give the corresponding amino-derivatives **3a–e**. The overall yields of the compounds **3a–e** are 80%–95%.[31,32]

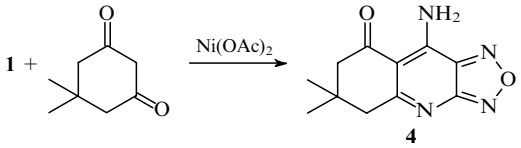


1 **2a–e** **3a–e**

$R^1 = R^2$ = Me (**a**); R^1 = Me, R^2 = Ph (**b**); $R^1 = R^2$ = Ph (**c**); R^1 = OEt, R^2 = Me (**d**); R^1 = OEt, R^2 = Ph (**e**).

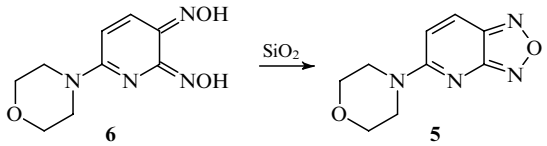
Even in the case where $R^1 \neq R^2$, as in the compound **2b**, the reaction occurs regioselectively giving only one product **3b** in which the more bulky substituent is attached directly to the pyridine ring.

The reaction of the nitrile **1** with dimedone in the presence of nickel acetate affords tricyclic compound **4** in 67% yield. In this case, the intermediate enamine was not isolated.[32]



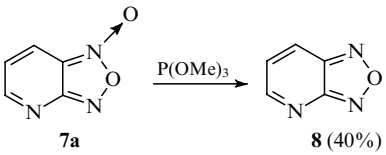
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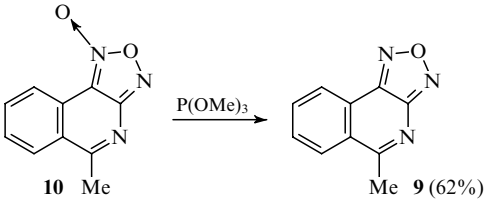
Dehydration of 1,2-dioximes (glyoximes) is used most widely for the synthesis of furazans.[1,6] An unusual version of dehydration has been employed in order to prepare furazan **5**. 2,3-Dihydroxyiminopyridine **6** adsorbed on silica gel undergoes spontaneous dehydration over a period of 12 h to give the compound **5** in 14% yield.[33]



6 **5**

Readily available furoxanopyridine **7a** can be reduced to the corresponding furazan **8** by a short-term heating to 100 °C in trimethyl phosphite.[23] Benzo-annelated derivative **9** can be obtained in a similar way from the furoxan **10**.[34]





The above furazanopyridines have been synthesised only recently. Meanwhile, the 1(3)-oxides of furazanopyridines of type **A** (furoxans) were first prepared more than 40 years ago.[35] The synthesis of these compounds is based on the ability of *o*-azido nitro aromatic compounds to undergo thermally induced intramolecular cyclocondensation. The mechanism of this transformation has been studied comprehensively by measuring the kinetics of this reaction for benzene derivatives.[11] It is believed that an oxygen atom of the nitro group attacks a nitrogen atom of the azide group. Cyclisation can be represented as electron transfer occurring synchronously with elimination of a nitrogen molecule.

Thus heating of tetrazolopyridine **11a**, which is formed upon treatment of chloropyridine **12a** with sodium azide, in dichlorobenzene leads to elimination of a nitrogen molecule from the intermediate azide **13a** and closure of the furoxan ring yielding the bicyclic compound **7a**.[35] Later it has been shown that the compound **7a** is formed in approximately the same yield when thermolysis is carried out in some other solvents or without a solvent (Table 1).

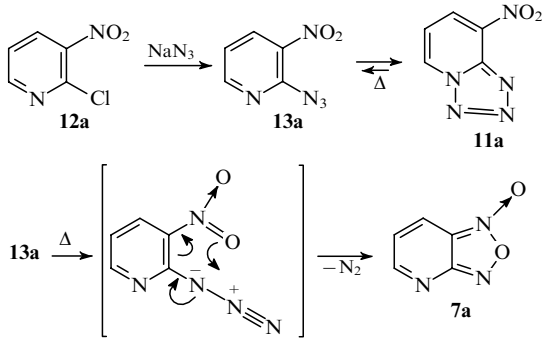
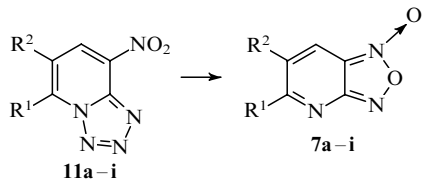


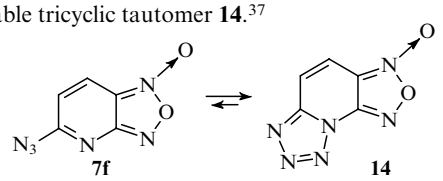
Table 1. Synthesis of furoxano[3,4-*b*]pyridines **7a**–**i** by thermolysis of the corresponding tetrazolopyridines **11a**–**i**.



Compound	R^1	R^2	Solvent	Temperature/ °C	Time/ h	Yield (%)	Ref.
11a	H	H	none	170	0.03	97	35
			PhOPh	175		75	36
			PhMe	110		96	37
			none	130	0.66	—	38
			dioxane	Δ		97	39
11b	H	Me	none	155	0.03	93	40
11c	H	COOH	none	161	0.03	86	40
11d	H	COOMe	"	106	0.03	97	40
11e	H	NO_2	"	130		—	37
			"	95	0.03	—	38
			PhMe	95		92	37
11f	N_3	H	MeCN	82	4	88	37
			C_6H_6	80	4	85	37
11g	$NPPh_3$	H	PhMe	110		75	37
11h	NHPic [a]		NO_2	AcOH	118		—
41							
11i	NH_2	NO_2	C_6H_6	80	1.5	95	42, 43

This reaction is general. The presence of any substituents, especially electron-withdrawing ones, in the initial nitrotetrazolopyridines **11a**–**i** facilitates their transformation into tautomeric 2-azido-3-nitropyridines and is thus favourable for the formation of the furoxan ring upon thermolysis (see Table 1).

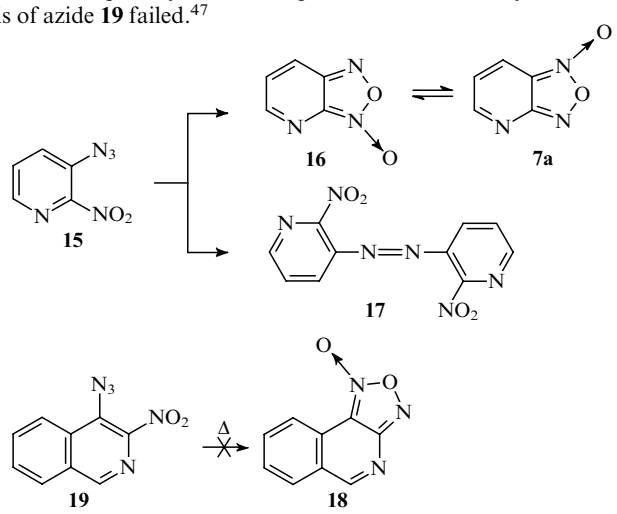
It should be noted that furoxanopyridine **7f** exists as the more stable tricyclic tautomer **14**.[37]



A particular modification of this method is the reaction of 2-chloro-3,5-dinitropyridine with sodium azide in the presence of phase transfer catalysts in dichloroethane followed by keeping the reaction mixture at 60 °C. The furoxanopyridine **7e** is prepared in this way in 92% yield without isolation of the intermediate azide or tetrazolopyridine.[44]

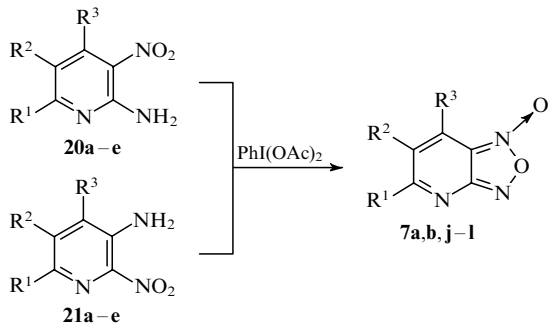
The thermolysis of azide **15**, isomeric to azide **13a**, gives the furoxanopyridine **7a**, which is thermodynamically more stable than isomer **16**.[45, 46] It is noteworthy that for the azide **15**, azido–tetrazole tautomerism is impossible, and in this case, the solvent determines not only the yield of the bicyclic compound **7a** but also the reaction pathway itself. A similar situation is observed in the transformation of *o*-azidonitrobenzenes into benzofuroxans.[11] Thus at 87 °C in decalin, the yield of the compound **7a** is 94%, while in ethanol, it is equal to 80%. Thermolysis of the azide **15** in *o*-dichlorobenzene or acetic anhydride does not give a furoxan derivative but yields instead azo compound **17**.[46]

An attempt to synthesise isoquinolinofuroxan **18** by thermolysis of azide **19** failed.[47]

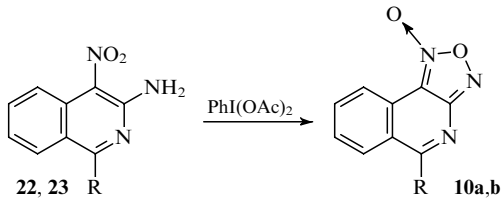


Yet another method for the synthesis of furoxano-[3,4-*b*]pyridines consists in oxidative condensation of 2(3)-amino-3(2)-nitropyridines. The most widely used oxidant which permits successful preparation of this bicyclic system is diacetoxy-λ^3-iodanylbenzene.[34, 36, 39, 48, 49] In fact, when amines **20a**–**e** or isomeric amines **21a**–**e**, or bicyclic amines **22** and **23** are merely stirred with this reagent in acetic acid, acetone or benzene at room temperature or at 50–60 °C, the corresponding furoxans **7** or **10a**,**b** are formed in 70%–90% yields.

The use of sodium hypochlorite as the oxidant in the synthesis of furoxano[3,4-*b*]pyridine derivatives usually does not lead to the desired products, unlike its use in the synthesis of benzofuroxans [11] from the corresponding *o*-amino nitro compounds.[36] Only one example of successful employment of this oxidant in the reaction in question is known. On treatment with sodium hypochlorite in a methanolic solution of KOH, the amine **23** undergoes

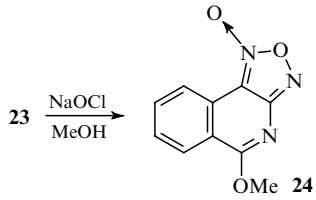


$R^1 = R^2 = R^3 = H$ (**a**); $R^1 = R^3 = H$, $R^2 = Me$ (**b**); $R^1 = R^2 = H$, $R^3 = Me$ (**20c**, **21c**, **7j**); $R^1 = Me$, $R^2 = R^3 = H$ (**20d**, **21d**, **7k**); $R^1 = R^3 = Me$, $R^2 = H$ (**20e**, **21e**, **7l**).

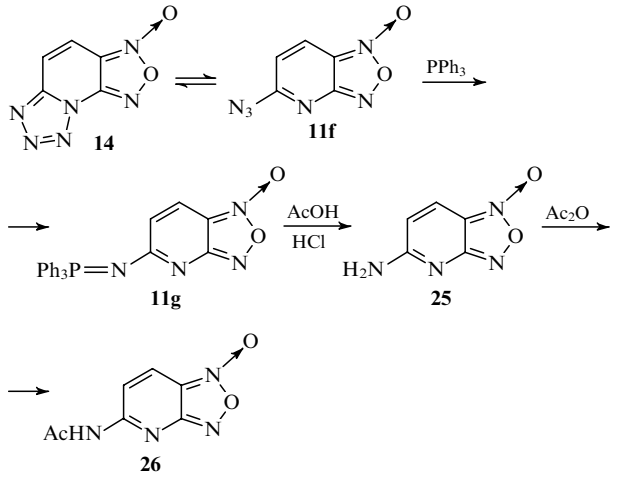


R = Me (**22**, **10a**), OC_6H_4Cl-*p* (**23**, **10b**).

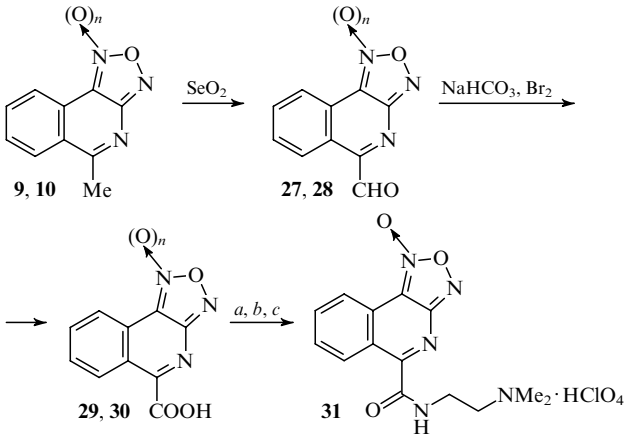
oxidative condensation with simultaneous replacement of the *p*-chlorophenoxy group by a methoxy group to give tricyclic compound **24** in 64% yield.[34]



Furazano[3,4-*b*]pyridines enter into two types of reactions. The first type comprises transformations that do not affect the bicyclic cage of the initial molecule. Reactions in which this cage is destroyed belong to the second type. The first type of reactions includes transformations of the functional groups present in the pyridine moiety of the molecule. Thus refluxing of the tetrazole **14** in ethanol in the presence of triphenylphosphine results in the formation of the iminophosphorane **11g** in 90% yield. Hydrolysis of this product occurs quantitatively and affords amine **25**, which is readily acylated with acetic anhydride to give amide **26**.[37]

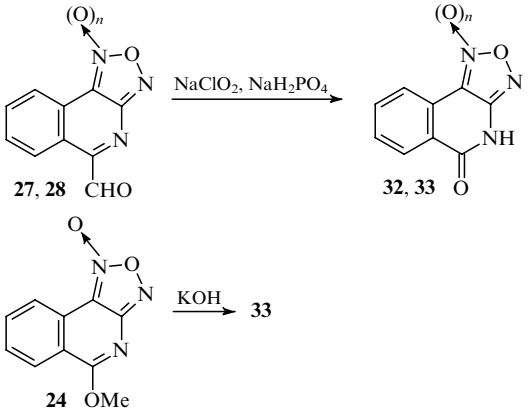


Refluxing of the tricyclic compounds **9** ($n = 0$) or **10** ($n = 1$) with selenium dioxide in dioxane is accompanied by oxidation of the methyl group. This gives aldehydes **27** and **28** in 56% and 75% yields, respectively.[34] Further oxidation of these products with bromine in a solution of sodium bicarbonate in aqueous butanol gives rise to the corresponding acids **29** (yield 72%) and **30** (yield 65%). The acid **30** was converted into amide **31**.[34]



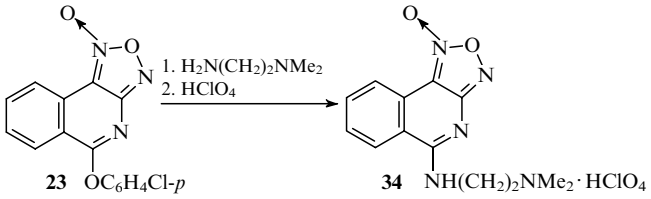
(*a*) Et_3N, BuOCOCl; (*b*) $H_2N(CH_2)_2NMe_2$; (*c*) $HClO_4$; $n = 0$ (**9**, **27**, **29**), $n = 1$ (**10**, **28**, **30**).

Interestingly, when sodium chlorite is employed as the oxidant in this reaction, the acid is not formed but instead the aldehyde group is eliminated and the C(5) atom in the ring is oxidised. The corresponding isoquinolinones **32** and **33** are produced in 75% – 79% yields. The compound **33** (yield 54%) can also be obtained by alkaline hydrolysis of the methoxy-derivative **24**.



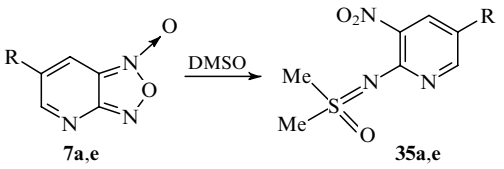
$n = 0$ (**27**, **32**), 1 (**28**, **33**).

Treatment of the *N*-oxide **23** with excess (*N*,*N*-dimethylamino)ethylamine at 75 °C leads to substitution of the *p*-chlorophenoxy group. The resulting amine **34** was isolated as the corresponding perchlorate in 42% yield.[34]

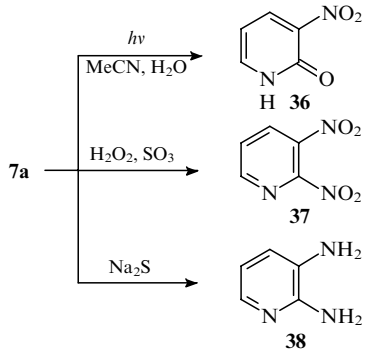


The second type of reaction typical of furazano[3,4-*b*]pyridine derivatives is transformation of the furoxan ring. For example, when the bicyclic derivatives **7a**,**e** are heated in dimethyl sulfoxide, retro-cleavage of the furoxan ring at the N – O bond occurs giving rise to a nitro group and a nitrene. The nitrene reacts with the solvent yielding sulfimine *S*-oxides **35a**,**e**.[38] Irradiation of the *N*-oxide **7a** with a UV lamp in aqueous acetonitrile for 30 h affords nitropyridone **36** in 18% yield.[33] The furoxan **7a** is not oxidised with *m*-chloroperbenzoic acid. However, treatment of **7a** with concentrated hydrogen peroxide in oleum results in oxidation of the furoxan ring giving 2,3-dinitropyridine **37** in 60% yield. No products resulting from the oxidation of the pyridine nitrogen

atom were detected. An additional nitro group present in the initial furoxan, for example in **7e**, makes the furoxan ring resistant to oxidation.[37]

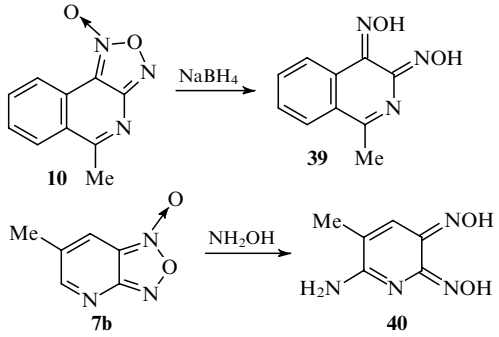


R = H (**a**), NO_2 (**e**).

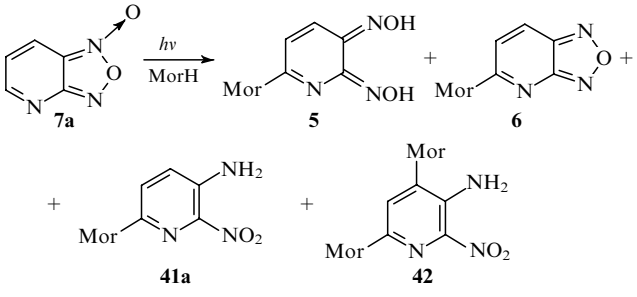


Diamine **38** has been obtained in 17% yield on treatment of the furoxan **7a** with sodium sulfide. It was suggested that the furazan **8a** could also arise in this reaction; however, it was not isolated in this study.[35]

On treatment with sodium borohydride at 50 °C in methanol, the furoxanisoquinoxaline **10** is reduced to give glyoxime **39** in a low yield.[34] The reduction of a furoxan ring giving two oxime groups occurs more efficiently under the action of hydroxylamine. Thus the reaction of the *N*-oxide **7b** with hydroxylamine affords glyoxime **40** in 54% yield. It should be noted that in addition to the reduction of the furoxan moiety, this reaction involves amination of the pyridine ring.[40]



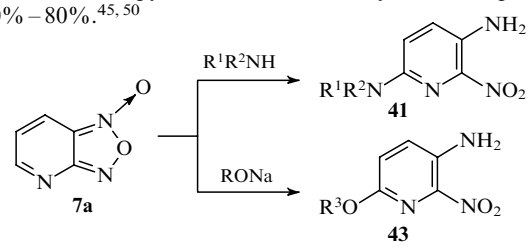
Photolysis of the compound **7a** (λ = 254 nm) carried out for 15 h in dichloromethane in the presence of morpholine under argon at room temperature gives a series of morpholine-containing products such as the glyoxime **6** (5%), the furazan **5** (9%), monomorpholylpyridine **41a** (0.3%) and bis(morpholyl)pyridine **42** (0.3%).[33]



Mor is morpholin-1-yl.

However, the compound **41** as well as a large number of its analogues can be prepared in a higher yield by conventional nucleophilic substitution. Treatment of the compound **7a** with N- and O-nucleophiles in water or ethanol at 18–25 °C induces opening of the furoxan ring accompanied by nucleophilic substitution of the hydrogen atom at C(6) in the pyridine ring.

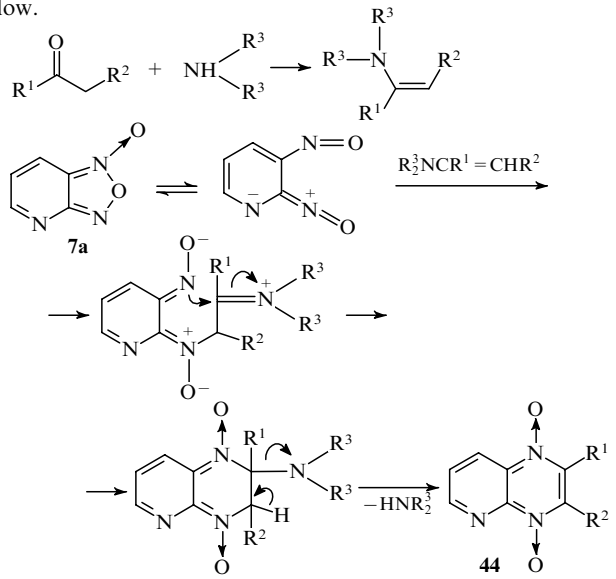
This reaction has been used to prepare a group of diverse 3-amino-2-nitropyridines **41** and **43**. The yields of the products are 70%–80%.[45, 50]



R^1–R^2 = $(CH_2)_2O(CH_2)_2$, $(CH_2)_2NH(CH_2)_2$, $(CH_2)_4$;
R^1 = R^2 = H, Me, Et; R^1 = H: R^2 = Me, Et, Bu; R^3 = H, Me, Et.

It is noteworthy that aminonitropyridines such as **41** and **43** as well as some other products of transformation of furoxanopyridines are potential precursors of polyfunctional derivatives of the same bicyclic system (which can be synthesised, for example, by oxidation). Unfortunately, this line of research is not represented in original publications.

The reaction of furoxanopyridines and amines in the presence of carbonyl compounds having an α-methylene unit follows a totally different pathway. In this case, the so-called Beirut reaction occurs,[11] in which enamine formed in the reaction medium functions as the active nucleophile, attacking the furoxan ring rather than the C(6) atom of the pyridine ring. The amine merely catalyses this transformation and is not incorporated in the reaction products, which are azaquinoxaline bis-*N*,*N*′-oxides **44**.[39, 51, 52] The mechanism proposed for this process is presented below.



R^1	Me	Me	H	Pr^i	Me
R^2	Me	H	Me	H	CO_2Me
R^1	CO_2Me	Me	Me	H	$CH(OMe)_2$
R^2	Me	$CONMe_2$	CH_2CO_2Me	$CH(OMe)_2$	H

Unlike benzofuroxans, the furoxanopyridine **7a** gives rise to the Beirut reaction products in low yields (20%–30%). The standard procedure is very simple and consists in stirring the furoxan **7a** with excess carbonyl compound in ethanol in the presence of an amine (ammonia, morpholine, pyrrolidine, *etc.*) or sodium acetate. The resulting azaquinoxaline bis-*N*,*N*′-oxides **44** are of interest for pharmacology.

Detailed analysis of the ^1H and ^{13}C NMR spectra has provided full assignment of all the ^{13}C and ^1H signals for furazano[3,4-*b*]pyridine derivatives.[23, 31, 37] NMR spectroscopy is especially useful for the investigation of isomeric *N*-oxides of this bicyclic system.[23, 49] The acid–base properties of the compound **7h** have been estimated based on the data of potentiometric titration in various solvents.[41] X-Ray diffraction analysis of the bicyclic furazan **3a** [31] and the tricyclic furoxan **14** [37] has shown that the bond lengths and bond angles in these compounds are close to the standard values. Kinetic studies led to the assumption that the initial events in the thermal decomposition of the compounds **7e** and **7i** and benzofuroxan and pyridine *N*-oxide derivatives are similar. These reactions were assumed to involve the formation of three-membered activated intermediates of the oxaziridine type.[53–55]

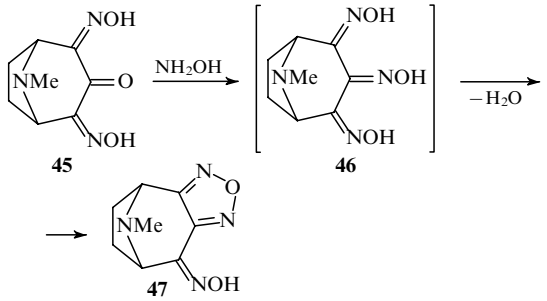
The furoxan **7a** has been patented as a modifier (vulcaniser) for unsaturated polymers.[56–59] Nitro-derivatives of this bicyclic system are thermally stable explosives.[42, 53, 54] Biological studies have shown that some furazanoquinoxalines exert moderate inhibitory effect on c-AMP-dependent protein kinase.[60]

2. Furazano[3,4-*c*]pyridines

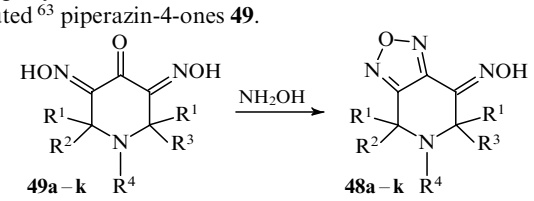
Derivatives of furazano[3,4-*c*]pyridine (**B**) are also referred to as 1,2,5-oxadiazolo[3,4-*c*]pyridines, and the corresponding *N*-oxides are also called furoxano[3,4-*c*]pyridines.

The methods used to synthesise this class of compounds are more diverse, while the procedures employed to prepare the *N*-oxides largely resemble those outlined above.

The first representative of furazano[3,4-*c*]pyridines — cage furazan **47** — was prepared 100 years ago by treatment of α,α′-dihydroxyiminotropinone hydrochloride **45** with an alkaline solution of hydroxylamine. Obviously, the reaction starts with oximation of the free carbonyl group, which is followed by dehydration of two neighbouring oxime groups in the trioxime **46** thus formed. Compound **47** was isolated in 90% yield.[61]



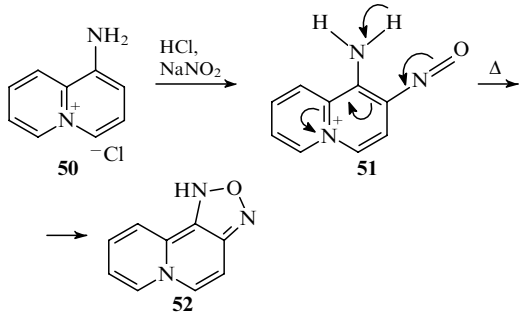
A series of fused furazan derivatives **48** have been obtained in high yields from 2,2,6,6-tetrasubstituted [62] and 2,6-disubstituted [63] piperazin-4-ones **49**.



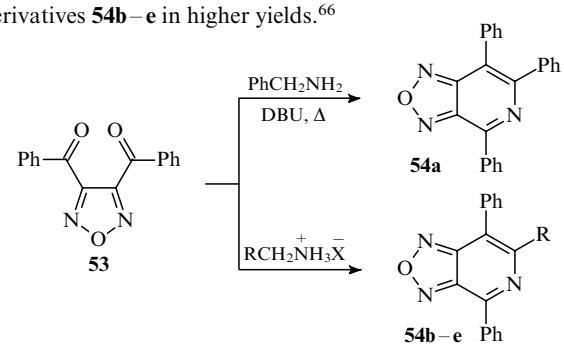
Compounds **48** and **49**	R^1	R^2	R^3	R^4
a	Me	Me	Me	H
b	Me	Me	Me	OH
c	H	Me	Me	Me
d	H	Me	Me	H
e	H	Me	Me	Bu^t
f	H	Ph	Ph	Me
g	H	Ph	Me	Me
h	H	Me	Me	OMe
i	H	H		Ph
j	H	H	H	Bu^t
k	H	H	H	H

When asymmetrical initial compounds are used, for example **49g,i**, mixtures of isomers are produced.

Nitrosation of quinolizinium salt **50** with sodium nitrite in 2 M hydrochloric acid affords *o*-amino nitroso compound **51**, which was reported [64] to be converted into tricyclic derivative **52** during recrystallisation from ethanol.

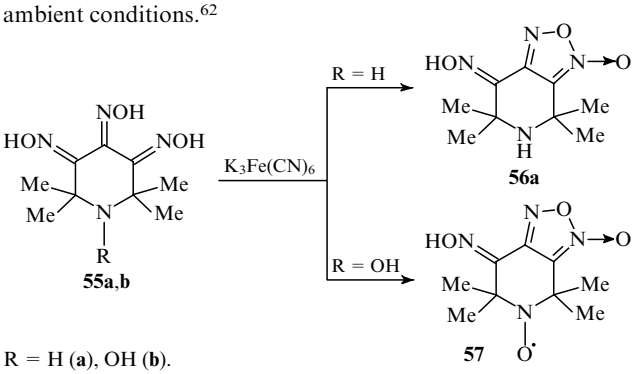


Furazano[3,4-*c*]pyridine derivatives have also been synthesised from furazan precursors. Thus condensation of 3,4-dibenzoylfurazan **53** with benzylamine in boiling toluene catalysed by diazabicycloundecene (DBU) results in the formation of compound **54a** in 13% yield.[65] However, condensation of dibenzoylfurazan with salts of amines having electron-withdrawing substituents at the α-carbon atom is more efficient and gives derivatives **54b–e** in higher yields.[66]



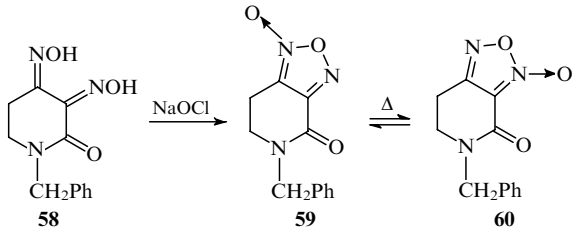
Compound	R	X	Yield (%)
54b	CO_2Et	Cl	41
54c	CO_2Me	Cl	45
54d	CN	HSO_4	73
54e	COPh	Cl	44

The reaction of trioxime **55a** with potassium ferricyanide occurs as oxidative cyclocondensation of two neighbouring oxime groups yielding furoxan **56a**. A similar treatment of the trioxime **55b** is accompanied by oxidation of the hydroxylamine function and gives rise to the furoxan nitroxide **57** stable under ambient conditions.[62]

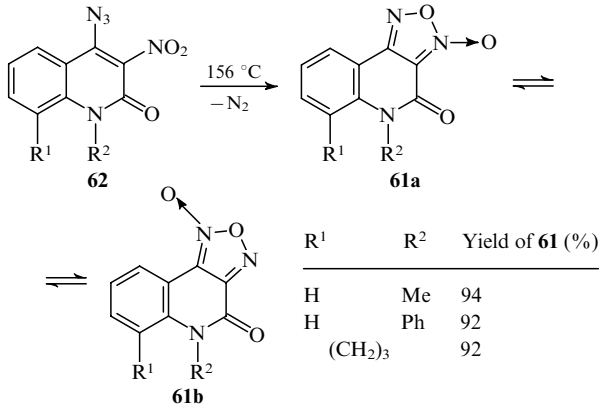


R = H (**a**), OH (**b**).

Oxidation of an alkaline solution of cyclic glyoxime **58** with sodium hypochlorite involves closure of the furoxan ring and gives lactam **59** in 87% yield.[67] On heating in toluene, this product partly rearranges to the isomeric 3-oxide **60**. The rearrangement gives a mixture of the isomers **59** and **60** in 1 : 4 ratio.

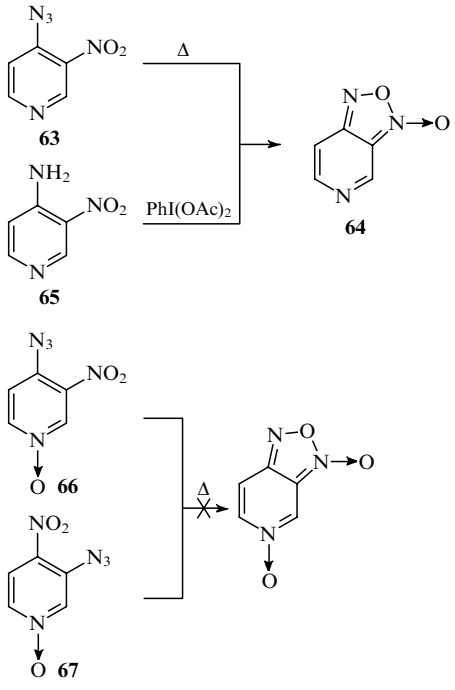


Benzoannelated analogues of the lactams **59** and **60**, for example **61**, have been synthesised by thermolysis of 4-azido-3-nitroquinolones **62** in boiling bromobenzene. The compounds **61** exist as unseparable mixtures of 3-oxides (**61a**) and 1-oxides (**61b**); this is clearly manifested in the ^{1}H NMR spectra.[68]



R^1	R^2	Yield of **61** (%)
H	Me	94
H	Ph	92
$(CH_2)_3$		92

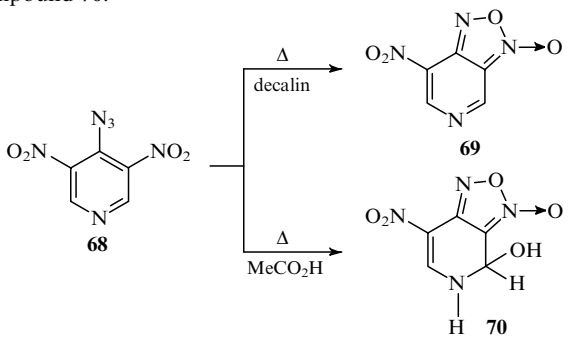
Thermolysis of 4-azido-3-nitropyridine **63** in boiling ethanol or decalin at 80 °C gives furoxan **64** in 74% and 95% yields, respectively.[46] It is worth noting that the earlier attempts to perform this reaction in boiling toluene have failed.[69]



When amine **65** is oxidised with diacetoxy-λ^3-iodanylbenzene, only traces of the *N*-oxide **64** are detected; when sodium hypochlorite is used as the oxidant, the product **64** is not formed at all.[36]

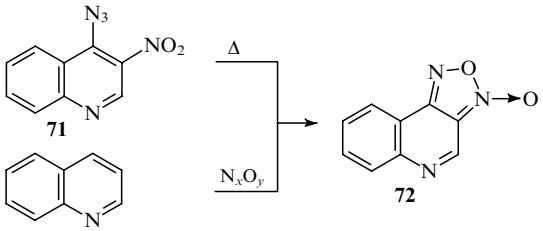
The attempts to annelate a furoxan ring to pyridine *N*-oxides have been unsuccessful. Thus thermolysis of *N*-oxides **66** and **67** gave only high-melting compounds, the structures of which were not identified.[69]

An additional nitro group present in the initial azidonitropyridine facilitates the formation of the furoxan ring. In this case, an unusual solvent effect is manifested. Thermolysis of compound **68** in decalin gives furoxan **69** in 97% yield.[46] When the process is carried out in benzene, the yield becomes 45% to 70%, the reaction product being produced as a complex with the solvent. The same reaction performed in acetic acid gives rise to hydrated compound **70**.[69]

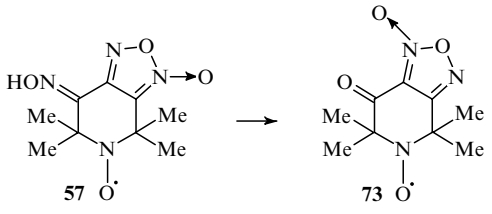


Being an analogue of dinitrobenzofuroxan,[11] the compound **69** might also exhibit superelectrophilic properties. However, no studies considering its reactivity from this viewpoint have been reported to date.

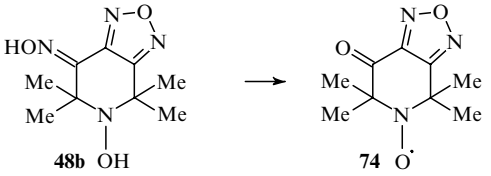
On heating in decalin, 4-azido-3-nitroquinoline **71** is smoothly converted into furoxan **72** in 94% yield.[46,47] The same compound is formed as a minor product, together with 3-nitroquinoline, when quinoline is treated with nitrogen oxides.[70]



Since the electron-withdrawing furazan ring in furazano[3,4-*c*]-pyridines is separated from the pyridine nitrogen, the N atom exhibits basic properties; hence, these compounds can form salts with acids.[69] Compounds in which the pyridine ring is hydrogenated show the highest basicity.[61] Conversely, the nitro derivative **69** is an acid; it forms salts with bases, hydrazine and transition metal cations and charge transfer complexes with naphthalene derivatives and pyrene (no data about the structure of complexes formed by **69** are presented in the study cited).[69] The oximes **47** and **48** can be acylated on treatment with acyl chlorides in the presence of bases according to a conventional procedure.[61,63] Deoximation of the nitroxide **57** is accompanied by simultaneous migration of the *N*-oxide oxygen atom in the furoxan ring to give ketone **73**.[62]

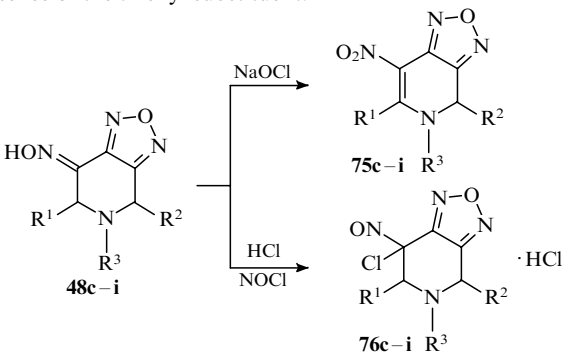


Oxidation of hydroxylamino oxime **48b** is accompanied by deoximation with generation of a radical site.[62] The furazan nitroxide **74** thus formed is stable under ambient conditions.



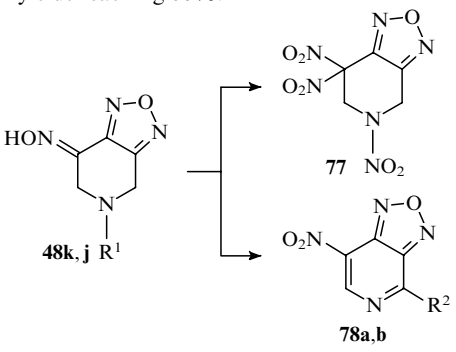
48b **74**

Treatment of the oximes **48c–i** with sodium hypochlorite in alkaline solutions affords nitro derivatives of dihydrogenated bicyclic compounds **75c–i**. However, the yields of these products are normally relatively low (12%–43%). The oximes **48c–i** are chlorinated with nitrosyl chloride in organic solvents to give chloro nitroso compounds, which have been isolated as salts **76c–h** in 60%–70% yields. The reaction of the compound **48i** with nitrosyl chloride affords the chloro nitroso derivative **76i**, its yield being only 7%, due to the side reactions caused by the presence of the thienyl substituent.[63]



48c–i **75c–i** **76c–i**

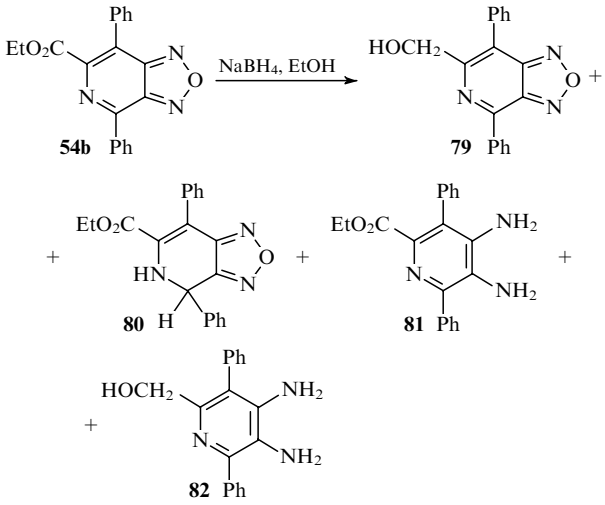
Nitration of the bicyclic compounds **48k** ($R^1 = R^2 = R^3 = H$) and **48j** ($R^1 = R^2 = H$, $R^3 = Bu^t$) with N_2O_4, N_2O_5, BF_4NO_2 or a mixture of HNO_3 with sulfuric or trifluoroacetic acid either gives trinitro derivative **77** or involves aromatisation giving rise to mono (**78a**) or di-nitro compound (**78b**). The reaction can be directed at the predominant formation of either of the products, their yields reaching 80%.[63]



48k,j **77** **78a,b**

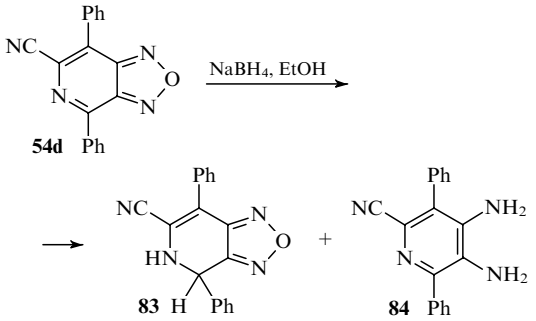
R^1 = H (**48k**), Bu^t (**48j**); R^2 = H (**78a**), NO_2 (**78b**).

The reduction of the compound **54b** with sodium borohydride involves three reaction sites — the ester group (to give hydroxymethyl derivative **79**), the pyridine ring (with the formation of dihydro derivative **80**) and the N–O bond (this leads to cleavage of the furazan ring resulting in the formation of diamines **81** and **82**). Depending on the reaction conditions (ratio of the reactants, temperature, reaction duration), a mixture of compounds enriched in a particular reduction product can be obtained.[71] The yields of individual compounds are rather low. When $LiAlH_4$ is used as the reducing agent, the reaction carried out at room temperature affords alcohol **79** in 62% yield.



54b **79** **80** **81** **82**

Only two types of products can be formed in a similar reaction of the cyano derivative **54d**. Stirring this compound with sodium borohydride in ethanol for 1 h at 20 °C gives furazan **83** in 65% yield and diamine **84** in a yield of only 4%. If the reaction mixture is refluxed for 10 min, the diamine **84** becomes the sole reaction product (yield 79%).[71]



54d **83** **84**

Treatment of the dihydro derivatives **80** and **83** with NaOH in ethanol (1.5 h, 20 °C) or with DBU in benzene (4 h) induces oxidative aromatisation giving rise to the compounds **54b,d** in good yields.[71]

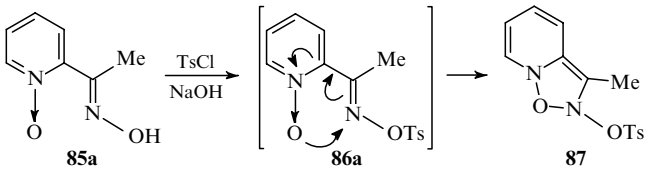
The structures of furazano[3,4-*c*] pyridine derivatives have been studied by mass spectrometry,[72,73] IR [71] and NMR [67] spectroscopy and UV spectrometry.[71]

The compound **54d** has been patented as a luminescent dye.[74]

3. Furazano[2,3-*a*]pyridines

Furazano[2,3-*a*]pyridines (**C**) are also referred to as 1,2,5-oxadiazolo[2,3-*a*]pyridines.

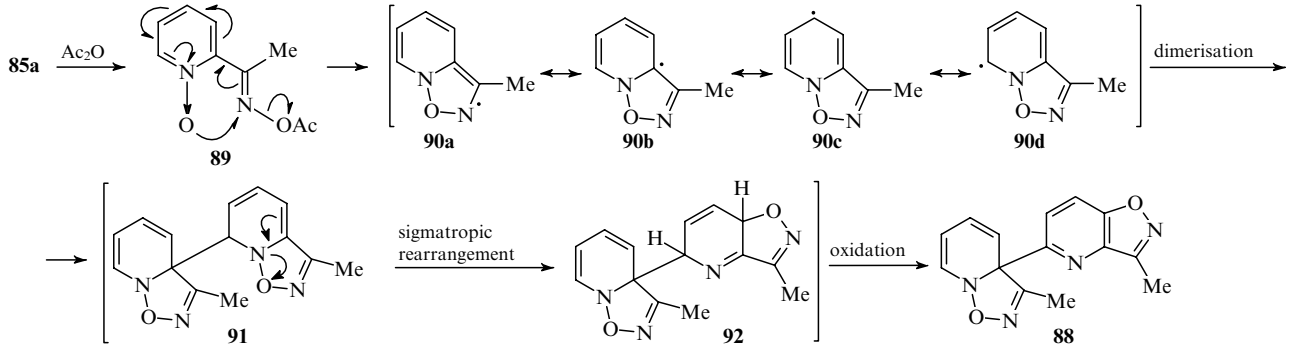
The only method for the synthesis of these compounds known to date is based on pyridine precursors. The reaction of the *E*-oxime of 2-acetylpyridine *N*-oxide **85a** with toluene-*p*-sulfonyl chloride in the presence of alkali leads on closure to a furazan ring and gives the bicyclic derivative **87** in 67% yield.[75]



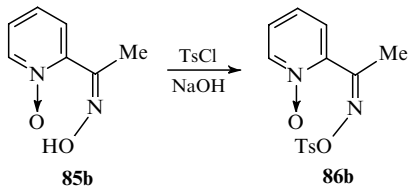
85a **86a** **87**

Presumably, this transformation involves the intermediate formation of the tosylate **86a**. A similar reaction of the corresponding *Z*-isomer **85b** does not give a bicyclic product but stops at the stage of formation of the tosylate **86b**.

Scheme 1

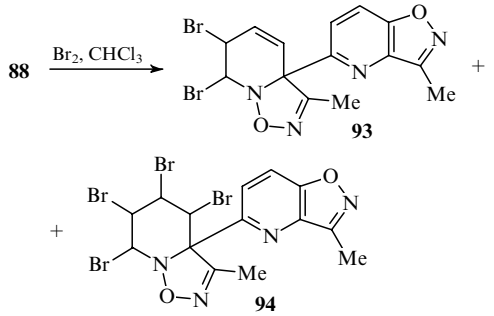


Treatment of the *E*- and *Z*-isomers of the methylquinolyl and methylisoquinolyl ketoxime *N*-oxides did not result in closure to give a furazan ring.[76]

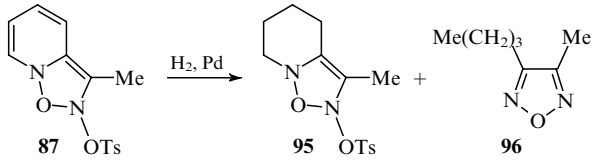


Heating of the *E*-isomer **85a** in acetic anhydride at 130 °C for 2 h affords furazan derivative **88** in 88% yield. At temperatures below 100 °C, the reaction stops at the stage of formation of acetyl derivative **89**. The *Z*-isomer **85b** is not converted into a furazan derivative even at high temperatures. The compound **88** is formed by a radical mechanism. This was confirmed experimentally by conducting the reaction in the presence of radical sources or radical traps. The course of the reaction can be described by a scheme with intermediates **90**–**92** (Scheme 1).[77]

The compound **88** remains unchanged when refluxed with 20% hydrochloric acid or alkali. However, it is readily brominated in chloroform to give a mixture of di- (**93**) and tetrabrominated (**94**) compounds in 52% and 33% yields, respectively. On refluxing in ether for 4 h, the compound **94** eliminates a bromine molecule, being quantitatively converted into the dibromide **93**.[77] The dimer **88** is stable against catalytic hydrogenation (H_2, Raney nickel).[77]



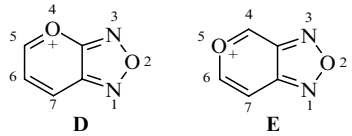
The tosylate **87** is reduced with hydrogen over Pd to give, depending on the reaction conditions, either hydrogenated bicyclic compound **95** (in a yield of up to 25%) or monocyclic furazan **96** (in a yield of up to 89%).[75]



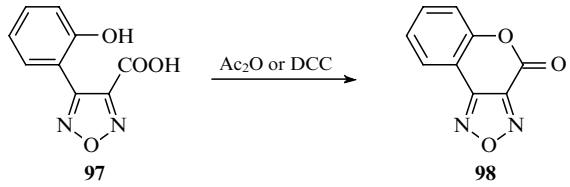
The structure of these derivatives, which are unusual for the furazan series, was established based on thorough analysis of their ^{1}H NMR, ^{13}C NMR, UV, IR and mass spectra; 2D NMR techniques have also been used for this purpose.[75,77]

IV. Furazanopyrans

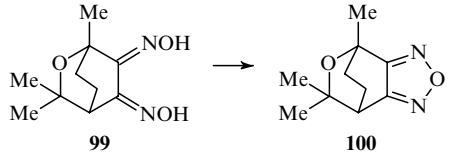
Of the two theoretically possible types of bicyclic compounds comprising furazan and pyran rings (**D** and **E**), only furazano[3,4-*c*]pyran derivatives (type **E**) are known.



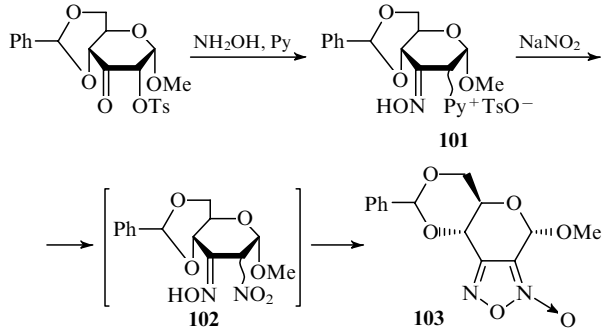
Furazano[3,4-*c*]pyran derivatives can be obtained both from furazan and pyran synthons. Thus treatment of furazan-3-carboxylic acid **97** with acetic anhydride or dicyclohexylcarbodiimide (DCC) induces intramolecular esterification. This gives lactone **98** in 80%–85% yield.[78]



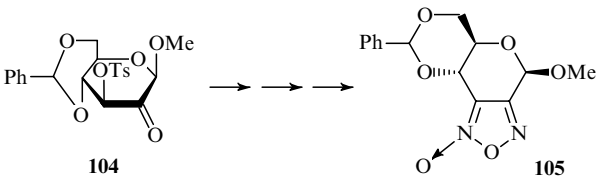
Dehydration of glyoxime **99** is accompanied by the formation of a furazan ring. This reaction gives cage furazan compound **100**.[79]



Refluxing of the pyridinium salt **101**, containing a carbohydrate fragment, with sodium nitrite in the presence of pyridine in aqueous THF leads to furoxan **103**, which is formed in 58% yield, apparently, *via* the intermediate formation of nitro derivative **102**.[80]

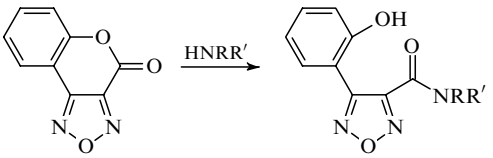


The isomeric furoxan **105** can be prepared by successive treatment of 2-keto-D-glucopyranoside **104** with hydroxylamine in aqueous pyridine and with a solution of sodium nitrite in aqueous dioxane followed by keeping the reaction mixture for 3 h at 90 °C. The yield of the furoxan **105** is 40%.[80]



104 **105**

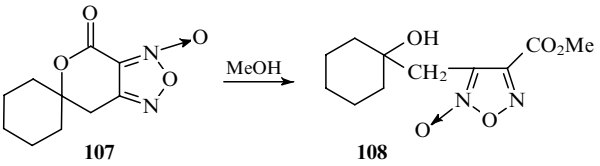
Data on the reactivity of furazano[3,4-*c*]pyran derivatives are very scarce. It is only known that the lactone ring in the compound **98** can be opened by amines to give amides of furazan-3-carboxylic acid **106**.[78]



98 **106a–c**

R = R′ = Me (**a**), Et (**b**); R = H, R′ = Ph (**c**).

Spirocyclic lactone **107** is cleaved on treatment with methanol, being thus converted into monocyclic furazan derivative **108**.[81]

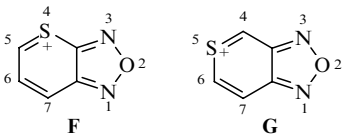


107 **108**

Compounds of this group have been characterised by the data of IR and UV spectroscopy and mass spectrometry.[80]

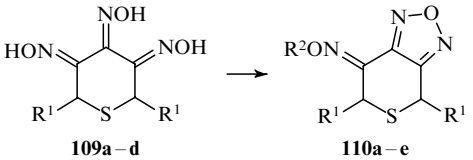
V. Furazanothiopyrans

Two types of furazanothiopyrans can be conceived, furazano[3,4-*b*]thiopyrans (**F**) and furazano[3,4-*c*]thiopyrans (**G**). However, no derivatives of structure **F** are known.



F **G**

Only one study concerning furazano[3,4-*c*]thiopyran derivatives has been published.[63] The dehydration of trioximes **109a–d** induced by heating with alkali or DCC is accompanied by closure to give a furazan ring, resulting in the formation of oximes **109a–d** in 67%–85% yields. The formation of a furazan ring with simultaneous acylation of the third oxime group was observed when trioximes **109b** and **109d** were treated with acetic anhydride. The acetates of bicyclic oximes **110d** and **110e** were isolated in 88%–93% yields.[63]



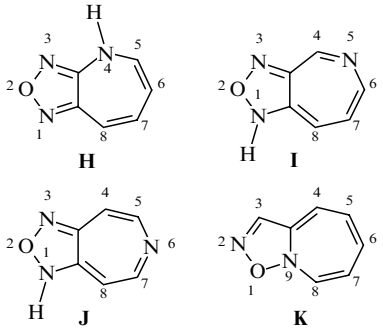
109a–d **110a–e**

$R^1 = R^2 = H$ (**a**); R^1 = Ph, R^2 = H (**b**); R^1 = Me, R^2 = H (**c**); R^1 = 2-furyl, R^2 = H (**109d**), Ac (**110d**); R^1 = Ph, R^2 = Ac (**110e**).

No data concerning the reactivity of this bicyclic system can be found in the literature.

VI. Furazanoazepines

Four types of annelation of furazan and azepine rings (**H**, **I**, **J** and **K**) are possible.

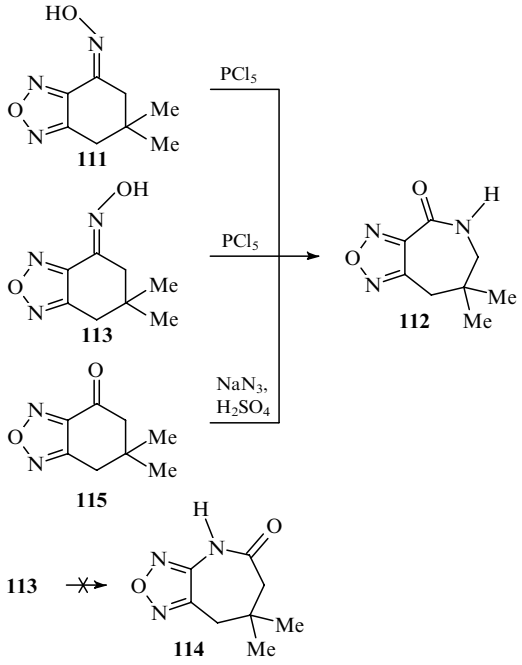


H **I** **J** **K**

Only few derivatives of furazano[3,4-*c*]azepine (**I**) have now been described.

The heterocyclic system of furazano[3,4-*c*]azepine has been mentioned in the literature as 1,2,5-oxadiazolo[3,4-*c*]azepine.

The Beckmann rearrangement of *Z*-oxime **111** in the presence of PCl_5 in ether at 20 °C gives rise to azepin-4-one **112** (yield 29%). Treatment of *E*-oxime **113** under similar conditions gives the same product **112** in a yield of only 5%. The main bulk of the initial compound is converted into a polymer rather than into the expected isomeric azepine **114**.[82]



111 **113** **112** **115** **114**

Azepine **112** is also formed upon the Curtius rearrangement of ketone **115**, induced by treatment with sodium azide in a mixture of chloroform and sulfuric acid. Note that the Curtius rearrangement gives the azepine **112** in a higher yield (55%) than the Beckmann rearrangement.[83]

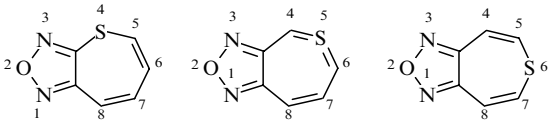
The reaction of **112** with acetyl chloride in the presence of sodium hydride in toluene gives the corresponding N-acetylation product in 67% yield.[82]

The structure of this azepine has been confirmed by the data of its IR, ^{1}H NMR and mass spectra.

The azepine **112** exhibits moderate antimicrobial activity.[83]

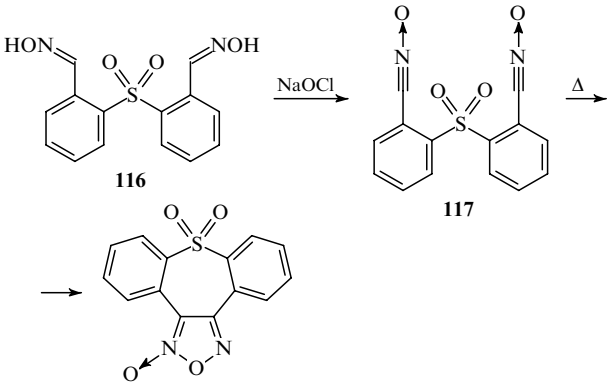
VII. Furazanothiepines

Of the three types of annelation of a furazan ring to a thiepine ring possible theoretically (**L**, **M** and **N**), only type **N** derivatives, furazano[3,4-*d*]thiepines, have been synthesised.



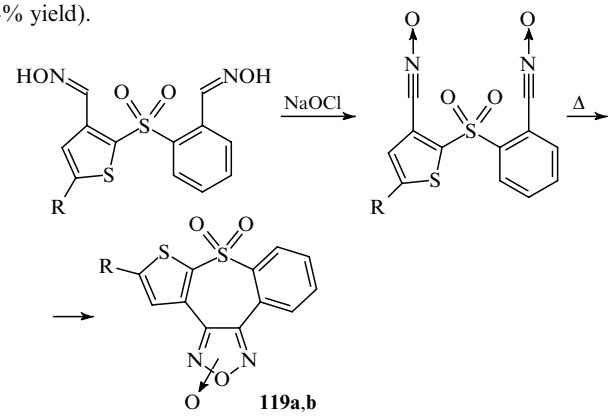
L **M** **N**

Heating of a benzene solution of bis-*N*,*N*-oxide **117**, prepared by treatment of dioxime **116** with an alkaline solution of sodium hypochlorite, affords furoxan **118** in 90% yield.[84]



116 **117** **118**

Thieno-annelated compounds **119a**,**b** have been synthesised in a similar way.[85] However, the replacement of a benzene ring in the initial molecule by a thiophene ring results in somewhat lower yields of the corresponding tetracyclic compounds **119a**,**b** (72% – 74% yield).



119a,**b**

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

Furoxans **119a**,**b** exist as unseparable mixtures of isomers.

VIII. Conclusion

The data presented in this review demonstrate on the one hand, the great synthetic potential of the class of compounds considered and, on the other hand, the scarcity of investigations along this line. The latter is apparently due to the facts that the required initial compounds are relatively difficult to obtain and that the methods for their transformations are not adequately developed. Meanwhile, some existing efficient methods for the construction of the title bicyclic systems have not yet found wide use. We hope that systematisation of the published data presented in this review will serve as the basis for the further development of this field of chemistry.

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