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Methods of synthesis of nitrogen-containing heterocycles using ureas and related compounds

A A Bakibaev, A Yu Yagovkin, S N Vostretsov

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Abstract. The review surveys numerous experimental data on the application of ureas in the synthesis of mono- and bi-cyclic nitrogen-containing heterocycles with the exception of pyrimidines and hydantoins. The methods of synthesis of phthalocyanines, diazepines, and diazocines from urea and its derivatives are also examined. The bibliography includes 220 references.

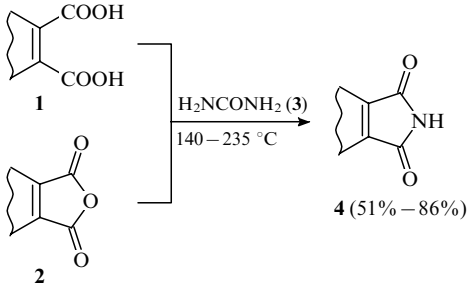
I. Introduction

The procedures of organic chemistry include nowadays a wide range of synthetic methods for the construction of azaheterocycles. Ureas are frequently used as the starting materials for this purpose, but, with the exception of studies describing the methods of synthesis of hydantoins [1–3] and pyrimidines,[4–10] there are no reviews in the literature surveying the extensive factual data on the methods of synthesis of nitrogen-containing heterocycles involving ureas. The purpose of the present review is to fill this gap. It does not include the methods of synthesis of hydantoins and pyrimidines except certain compounds of these classes where a non traditional approach to their synthesis has been employed.

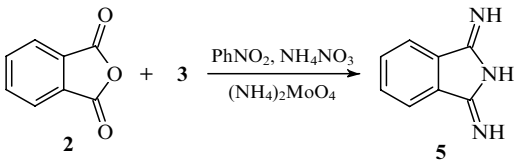
II. Methods of synthesis of monocyclic azaheterocycles

1. Synthesis of heterocycles containing one nitrogen atom

One of the convenient methods for the preparation of the cyclic imides **4** with a wide variety of structures is the pyrolysis of the dicarboxylic acids **1** or their anhydrides **2** in the presence of a slight excess of urea **3**.[11–16]



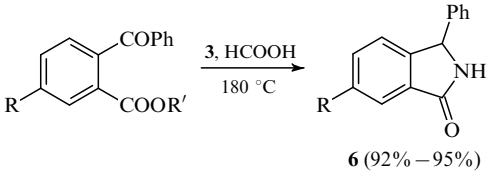
The early studies devoted to the synthesis of the imide **4** have been described in a review.[17] Although the pyrolysis of the anhydrides **2** proceeds in the vast majority of cases under milder conditions (140 – 185 °C) than the pyrolysis of the dicarboxylic acids **1** (185 – 235 °C), the yields of like imides are comparable. It is generally known that, when dicarboxylic acids are used in these reactions, the anhydrides **2** are formed initially. Under the influence of the products of the thermal decomposition of urea (NH_3 and HNCO), the latter are converted into the target imides **4** *via* recyclisation – cyclisation stages. In order to increase the effectiveness of the process, it is recommended that the pyrolysis of aromatic dicarboxylic acids **1** be carried out in ethylene glycol,[18] while that of the anhydrides **2** should be performed in xylenes, which readily remove water in the form of an azeotropic mixture.[16] The methods for the aminolysis of the anhydrides **2** by urea are suitable for the synthesis of diimides [19,20] and 3-dichloromaleimides.[21] We may note that in the latter case the reaction does not involve the fairly mobile chlorine atoms. (^{15}N)Homophthalimide has been synthesised by the reaction of (^{15}N)urea and homophthalic anhydride and was then converted into 1,3-dibromo- (2-^{15}N)isoquinoline by treatment with PBr_3 and $POBr_3$ (180 °C, 2 h).[22] According to patent data,[23] the interaction of phthalic anhydride **2** with urea in the presence of the $(NH_4)_2MoO_4$ catalyst at 210 °C leads to a 75% yield of 1,3-diiminoisoindoline **5** after 30 min.



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The reductive amination of 2-benzoylbenzoic acids or their esters with urea in formic acid (a modified Leuckart reagent) is completed by the formation of the dihydroisoindolinones **6**, characterised by a broad spectrum of biological activity.[24]

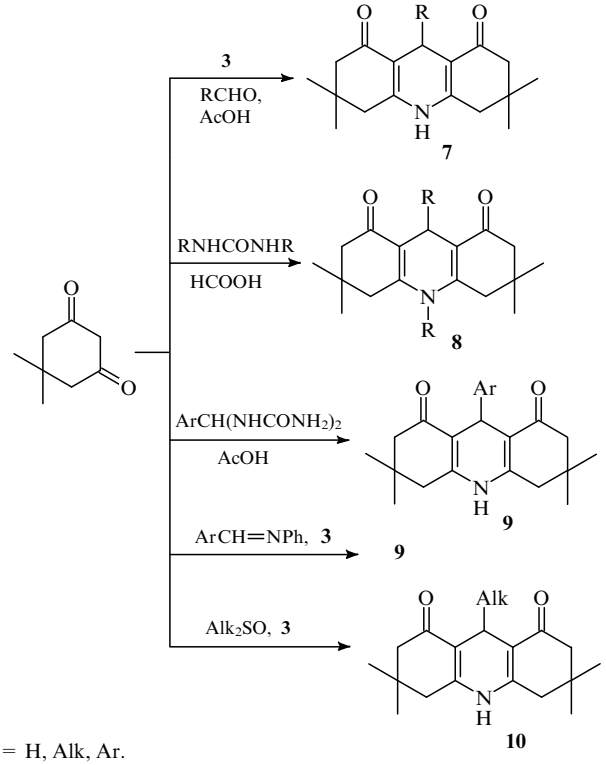


6 (92% – 95%)

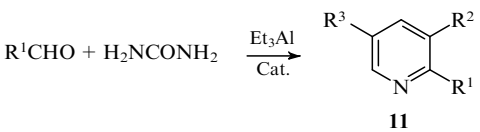
R = H, Cl; R′ = H, Me, Et.

The decahydroacridine-1,8-diones **7** – **10** (Scheme 1) can be readily obtained from 5,5-dimethylcyclohexane-1,3-dione (dimedone) and ureas in formic acid,[25–27] in acetic acid in the presence of aldehydes,[26] in dimethyl sulfoxide (DMSO) in the presence of azomethines,[28] with participation of dialkyl sulfoxides,[29] or by the reaction of dimedone with arylidenebisureas in glacial acetic acid.[30]

Scheme 1



R = H, Alk, Ar.



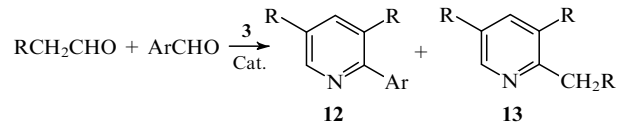
R^1, R^2, R^3 = Alk.

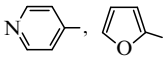
Depending on the structure of the substrates and the ureas, it is possible to obtain with the aid of these reactions the hydrogenated acridine-1,8-diones **7** – **10** with substitutents either in the 9-position (compounds **7**, **9**, and **10**) or in the 9- and 10-positions in the acridine ring (compounds **8**). It had been established [26,28] that the reactions of acyclic 1,3-dicarbonyl compounds with urea afford, together with the pyrimidinones which are traditional for reactions of this kind, also 3,5-disubstituted 1,4-dihydropyridines. Under these conditions, dihydropyridines are formed in larger amounts in a neutral or weakly basic medium [28] than in an acid medium.[26]

It has been observed comparatively recently that trisubstituted pyridines **11** – **13** are formed on liquid-phase condensation of aldehydes with urea in the presence of metal complex catalysts.[31,32] Thus, 2,3,5-trisubstituted pyridines **11** have been synthesised on heating aliphatic aldehydes with urea in an autoclave up to 200 °C in the presence of triethylaluminium and cobalt di(2-ethylhexanoate) as the catalyst (see Scheme 1).[31]

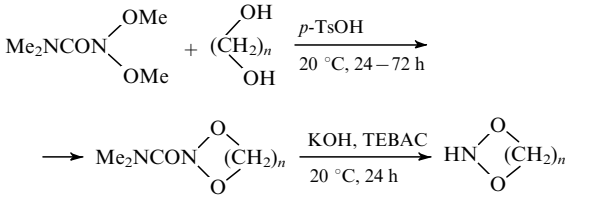
The mixed condensation of benzaldehyde with butyraldehyde and urea under analogous conditions makes it possible to obtain 3,5-diethyl-2-phenylpyridine in ~83% yield and with a high selectivity.[31]

The liquid-phase condensation of aliphatic C_4 – C_8 aldehydes with aromatic aldehydes and urea in the presence of metal complex catalysts, obtained by reducing cobalt 2-ethylhexanoate or Co, Al, Ni, V, Cu, Pd, Ti, Zr, *etc*. acetylacetonates with the aid of AlR_3, BR_3, or MgR_2 leads to the aryl- and heteroaryl-substituted pyridines **12** and **13**.[32] The composition of the reaction mixture and the yield of the reaction products depend on the structure of the initial aldehydes and the catalyst.



R = Alk; Ar = Ph, 4-$NO_2C_6H_4$, , 2-HOC_6H_4, 2-FC_6H_4, 2-$MeOC_6H_4$.

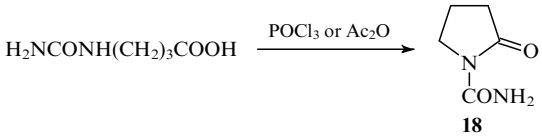
The reactions of 1,1-dimethoxyureas with ethylene glycol and propane-1,3-diol in the presence of toluene-*p*-sulfonic acid lead to 2,2-dimethylcarbamoyl-1,3,2-dioxazolidine **14** and 2,2-dimethylcarbamoylperhydro-1,3,2-dioxazine **15** respectively. On hydrolysis in the KOH-benzyltriethylammonium system, the latter afford 1,3,2-dioxazolidine **16** and perhydro-1,3,2-dioxazine **17**.[33]



14, **15** (27% – 55%) **16**, **17** (61% – 66%)

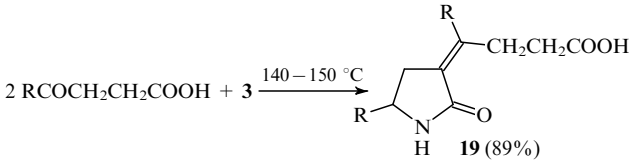
n = 2 (**14**, **16**), 3 (**15**, **17**); TEBAC = $Et_3BnN^+Cl^-$.

The cyclisation of 4-ureidobutanoic acid either in the presence of phosphorus oxide chloride under an inert atmosphere [34,35] or on treatment with acetic anhydride [36] leads to the pyrrolidinone **18**.



18

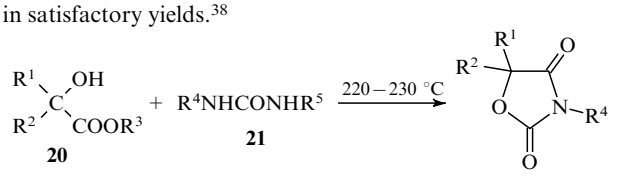
The azacyclisation of β-aroylpropionic acids on treatment with urea makes it possible to obtain substituted 4-pyrrolidin-2-ones **19** in high yields.[37]



R = Ph, 4-BrC_6H_4, tetralinyl.

High-temperature (160 – 230 °C) reactions of ureas with 1,2-bifunctional compounds, one of the functional groups of which is OH, constitute a fairly general method of synthesis of oxazolinones and oxazolidinones. Thus heating of the α-hydroxyesters **20**

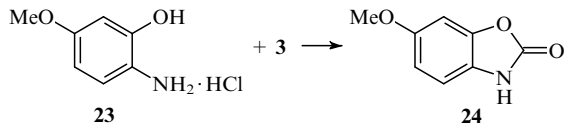
with 1,3-disubstituted ureas **21** affords the oxazolidine-2,4-diones **22** in satisfactory yields.[38]



20 **21** **22** (75% – 85%)

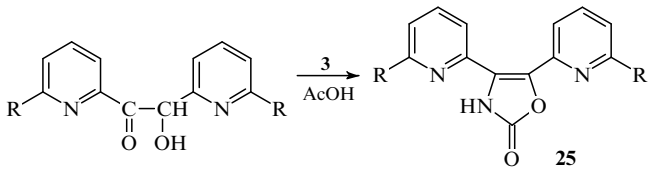
R^1, R^2 = H, Alk (C_1–C_4); R^3 = Alk (C_1–C_{10}); R^4 = R^5 = H, Ar.

Fusion of 2-amino-5-methoxyphenol hydrochloride **23** with urea leads to 6-methoxybenzoxazolin-2-one **24**.[39]



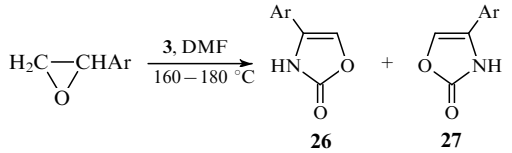
23 **24**

In contrast to other acyloins, 1,2-pyridoins afford predominantly substituted 4,5-bis(2-pyridyl)-4-oxazolin-2-ones **25** on heating with urea in glacial acetic acid.[40]



25

Aryloxiranes undergo interesting reactions on heating with urea without a solvent or in dimethylformamide.[41] The reaction is kinetically controlled: electron-donating substituents in the *ortho*- and *para*-positions of the phenyl group promote the preferential formation of the 5-aryloxazolin-2-ones **27** while electron-accepting substituents promote the formation of 4-aryloxazolin-2-ones **26**.

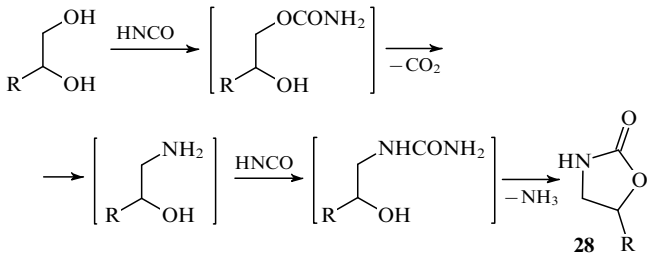


26 **27**

The reactions of vicinal diols with urea, leading to 5-R-oxazolidin-2-ones **28** have been investigated.[42–44] Compounds **28** can also be readily obtained from the monoesters of glycerol,[42,43] 3-aminopropane-1,2-diol,[42] and 2,3-epoxypropane-1,2-diol.[43]

The formation of the oxazolidinones **28** from diols and related compounds apparently proceed *via* a series of consecutive stages, presented in Scheme 2.[42]

Scheme 2

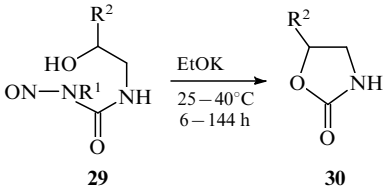


28

R = ArO, NH_2.

Since these reactions take place above the melting point of urea (under these conditions, it begins to undergo thermal decomposition into NH_3 and isocyanic acid [45]), the nature of the carbamoylating reagent in Scheme 2 is evident. As regards one of the key stages in the Scheme, namely the decarboxylation stage, it too is entirely unambiguous, since the tendency of carbamates to decarboxylate at elevated temperatures is generally known.

After treatment of 3-(2-hydroxyalkyl)-1-nitrosoalkylureas **29** with bases the oxazolidin-2-ones **30** were isolated in 73% – 96% yields.[46]

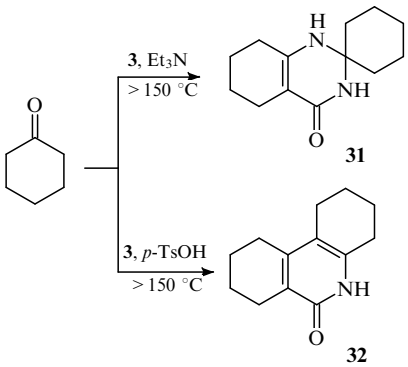


29 **30**

R^1 = Me, Et; R^2 = H, Me.

It has been postulated that the reaction begins with the intramolecular nucleophilic attack by the hydroxy-group on the electrophilic carbon atom of the carbonyl group. The intermediate hemiacetal decomposes into the oxazolidinone **30** and the intermediate $R^1N{=}NO^-K^+$.

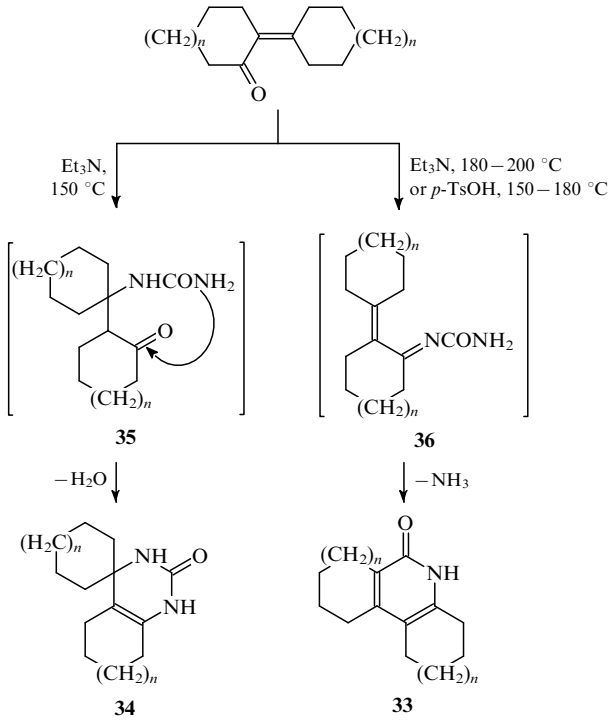
The high-temperature reaction of cyclohexanone with urea in triethylamine makes it possible to synthesise the spiro-compound **31**, whilst in the presence of toluene-*p*-sulfonic acid, decahydrophenanthridinone **32** is formed.[47–49]



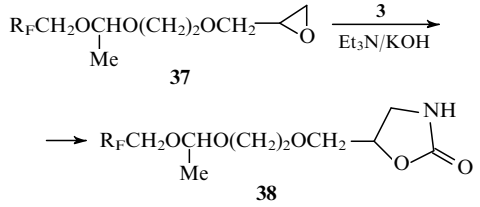
31 **32**

The condensation of urea with α,β-unsaturated ketones in acid (HCl, 60 °C) or basic (NEt_3, 150 °C) media leads to substituted 2-oxatetrahydro-pyrimidines.[50,51] It has been observed [52] that, on heating of 2-cyclohexylidenecyclohexanone and 2-cyclopentylidenecyclopentanone to 150 °C in triethylamine, the pyridinones **33** are formed only in trace amounts. They are the main products when the reaction is carried out at a higher temperature in the presence of NEt_3 or toluene-*p*-sulfonic acid.

The azaheterocycle **33** becomes the main product when the reaction is carried out at higher temperatures (180 – 200 °C) in the presence of triethylamine or toluene-*p*-sulfonic acid. The tetrahydropyrimidinone **34** is formed as a result of the nucleophilic Michael addition of urea to the double bond of the α,β-unsaturated ketone with subsequent dehydration of the alkylurea **35**. On the other hand, the pyridones **33** are apparently formed *via* the deamination of the intermediate **36**.

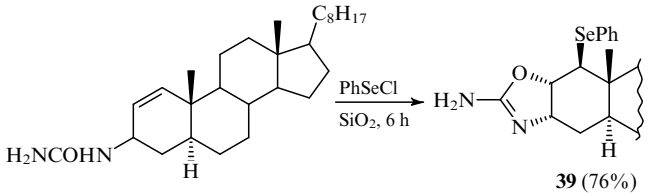


The regioselective opening of the epoxide ring in the epoxide **37**, containing the polyfluoroacetal group, by urea in a basic medium leads to the creation of the oxazolidine ring. Compounds **38**, formed under these conditions, are new functional fluorine-containing monomers.[53]

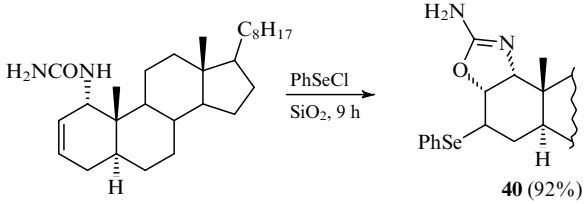


$R_F = H(CF_2)_n$; $n = 2-8$.

A series of studies [54–58] have been devoted to the intramolecular cyclisation of unsaturated ureas initiated by various catalysts. A method of synthesis of 4,5-dihydrooxazoles **39–44** from allylureas by intramolecular heterocyclisation, initiated by phenylselenyl chloride and catalysed by silica gel under an inert atmosphere, has been described.[54]

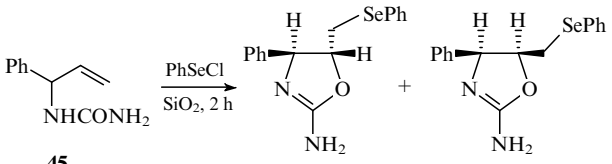


39 (76%)

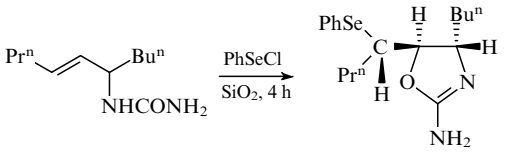


40 (92%)

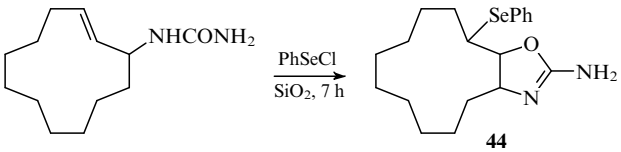
The formation of a mixture of diastereoisomers of the oxazolines **41** and **42** with a twofold excess of the *trans*-isomer **41** is the stereochemical outcome of the intramolecular cyclisation of the terminal alkenylurea **45** with participation of PhSeCl.[54]



45 **41** (64%) **42** (32%)

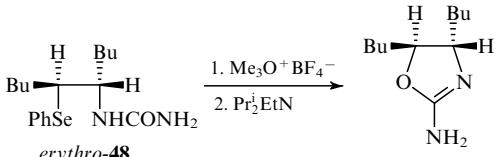


43 (81%)

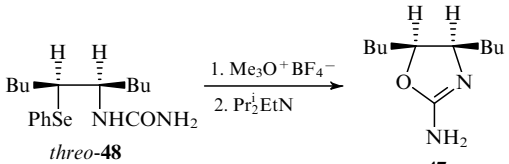


44

2-Aminooxazolines **46** and **47** are also formed stereospecifically from phenylselenylurea **48** in the presence of bases. Under these conditions, the *trans*-oxazoline **46** is formed from the *erythro*-isomer, while the analogous treatment of the *threo*-isomer leads to the *cis*-oxazoline **47**.[54]

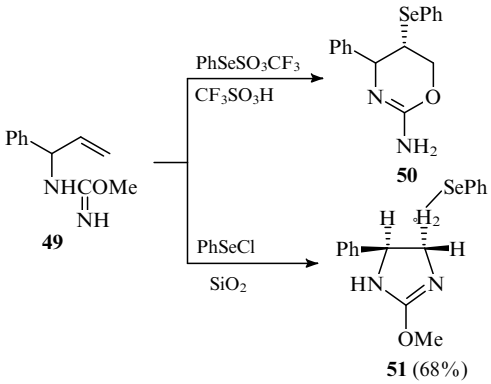


erythro-**48** **46** (93%)



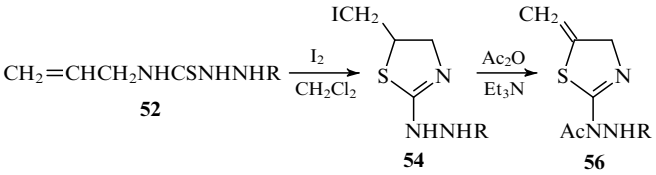
threo-**48** **47**

Allylisourea **49** interacts with organic selenium compounds under an inert atmosphere. Depending on the reaction conditions, it cyclises with formation of either the dihydro-1,3-oxazine **50** or the imidazoline **51**.[55]

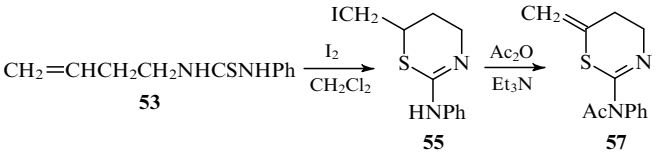


51 (68%)

N-Alkenylthiosemicarbazides **52** and the thioureas **53** readily undergo iodocyclisation to compounds **54** and **55** in methylene chloride. Their subsequent treatment with Ac_2O in triethylamine affords 2-R-1,3-thiazolines **56** and 2-(*N*-phenylacetamido)dihydro-1,3-thiazine **57** with an exocyclic methylene group.[59]

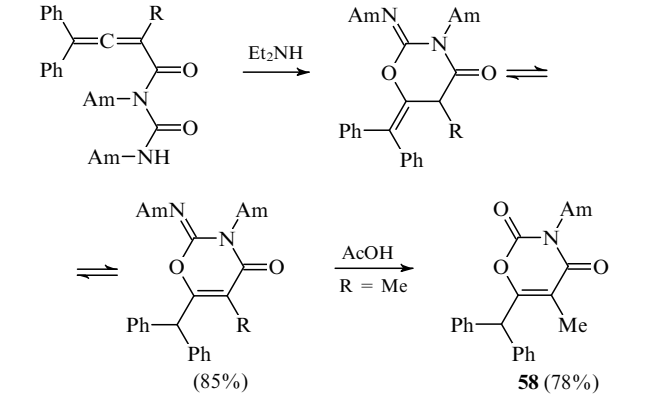


R = H, Ph.



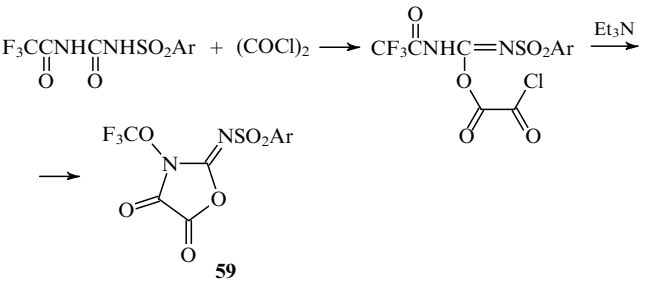
The cyclisation of 1-allyl-3,3-diethylthiourea to 2-diethylamino-5-iodomethyl-1,3-thiazoline on treatment with iodonium nitrate in the presence of pyridine proceeds without the retention of the exocyclic methylene group.[59]

The intramolecular cyclisation of allenic acylureas on treatment with diethylamine, *via* a series of intermediate stages, opens a path to tetrahydro-1,3-oxazine-2,4-diones **58** which are difficult to obtain.[60]

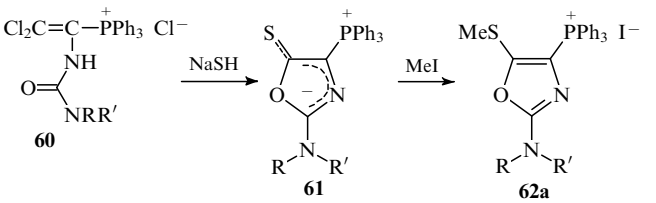


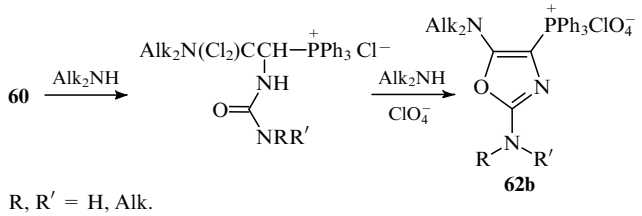
R = Me, Ph; Am = C_5H_{11}-n.

It has been established that the reactions of *N*-arenesulfonyl-*N′*-trifluoroacetylureas and oxalyl chloride under severe conditions in the presence of triethylamine are completed by the formation of 1,3-oxazolidine-4,5-diones **59**.[61]



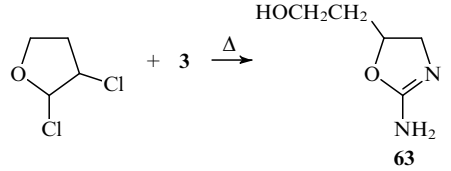
The cyclisation of phosphorylated *N*-(2,2-dichlorovinyl)ureas **60** to phosphorylated mesomeric betaines **61** and oxazoles **62a**,**b** proceeds in an interesting manner.[62]



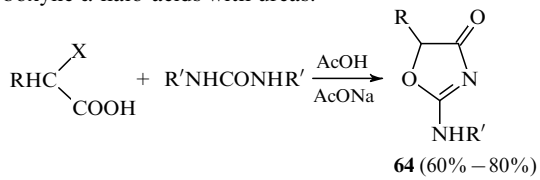


R, R′ = H, Alk.

On heating with urea, 2,3-dichlorotetrahydrofuran gives rise to 2-amino-5-(2-hydroxyethyl)oxazoline **63**.[63] The reaction proceeds *via* the opening of the furan ring with subsequent cyclisation of the intermediate substituted urea.

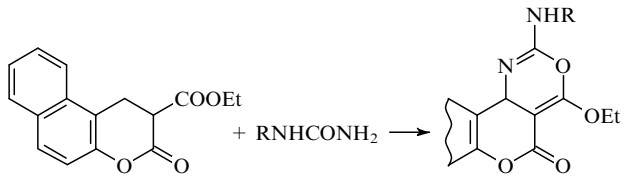


Ureides, which on refluxing in AcOH afford 2-aryl(cycloalkyl)amino-4-oxazolinones **64**, are obtained by the interaction of carboxylic α-halo-acids with ureas.[64]



X = Cl, Br;
R = H, Ph; R′ = H, Ar, cyclo-Alk.

The oxazines **65** have been obtained in satisfactory yields in the study of the reactions of 3-ethoxycarbonyl-5,6-benzocoumarin with monosubstituted ureas.[65]



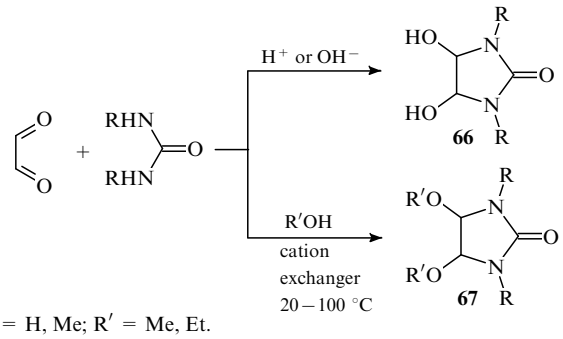
R = H, Alk, Ar.

The photocyclisation of acryloylureas (Hg lamp, 450 W, Pyrex, argon) leads to the formation of *N*-substituted azetidin-2-one derivatives.[66]

2. Synthesis of heterocycles containing two nitrogen atoms

a. Reactions of ureas with 1,2-bifunctional compounds

The azaheterocycles containing two nitrogen atoms are represented mainly by imidazole derivatives. The reactions of ureas with 1,2-bifunctional compounds proceed as a rule in polar solvents at temperatures below the decomposition temperature of urea (< 132.5 °C) and afford imidazolidinones (compounds with a carbamide fragment in the ring). Thus the interaction of equimolar amounts of urea and glyoxal in an alkaline or acid medium leads to 4,5-dihydroxyimidazolidin-2-ones **66**.[67–69] The 4,5-dialkoxy-derivatives **67** are formed in the reactions of ureas with glyoxal in alcoholic solutions in the presence of cation exchangers.[70]

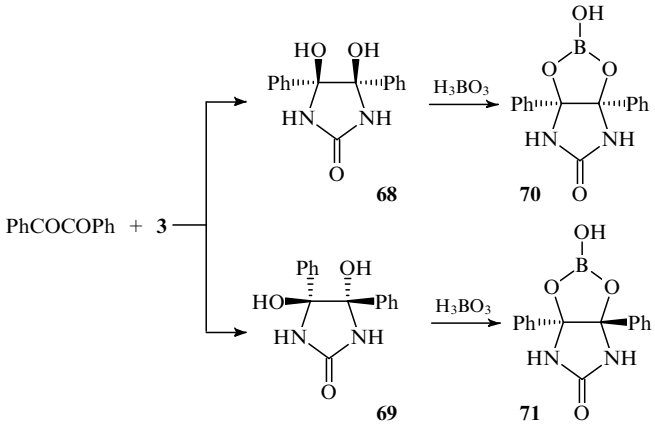


R = H, Me; R′ = Me, Et.

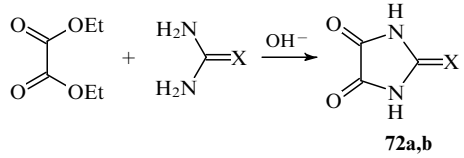
The vicinal diols **66** and their ethers **67** are convenient starting materials for the synthesis of a wide variety of bicyclic heterosystems and, what is especially important, for the synthesis of bicyclic compounds with an asymmetric structure.[71] In the acid-catalysed reaction with an equimolar amount of ureas, aromatic 1,2-diketones afford 4,5-diaryl-4,5-dihydroxyimidazolidin-2-ones.[72, 73]

It was later established that a mixture of the *cis*- and *trans*-isomers of 4,5-dihydroxyimidazolidinones **68** and **69** is formed in the reactions of 1,2-dicarbonyl compounds with ureas.[74]

It has been shown on the basis of ^{13}C and ^{15}N NMR spectroscopic and chromatographic data that the interaction of benzil with urea leads to mixture of the *cis*-diols **68** and *trans*-diols **69** in proportions of 65 : 35. The formation of the cyclic boric acid esters **70** and **71** has been used successfully for the separation of the diastereoisomers of such diols.[75]

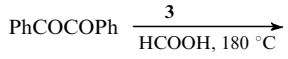


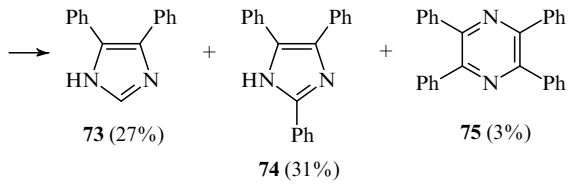
When urea or thiourea is heated with oxalic acid esters, parabanic acid **72a** or its 2-thio-analogue **72b** are formed respectively.[76]



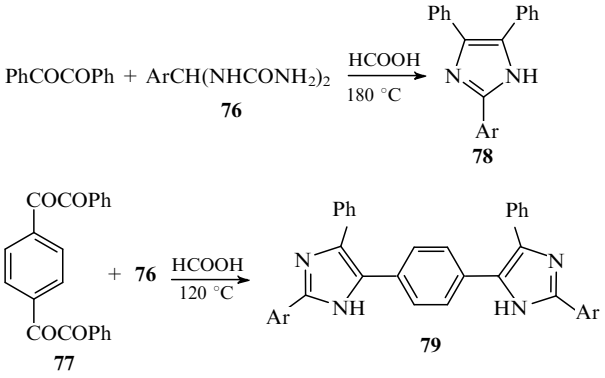
X = O (**a**), S (**b**).

The reaction of benzil with urea in formic acid at a high temperature leads to a mixture of the imidazoles **73** and **74** and tetraphenylpyrazine **75**.[77]

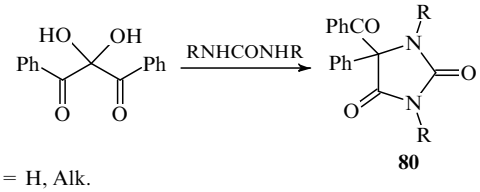




The arylidenebisureas **76**, known as the starting materials for the synthesis of pyrimidines, afford exclusively 2-aryl-4,5-diphenylimidazoles **78** and phenylenebisimidazolines **79** in their reactions with benzil in formic acid or with the tetraketone **77** in acetic acid respectively.[77, 78]

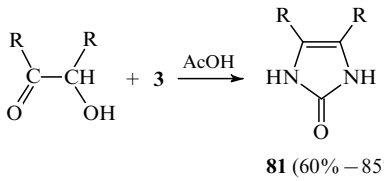


The hydrate of diphenylpropanetrione reacts with ureas in an acid or neutral medium to form the hydantoin derivatives **80**,[79] although the latter are usually obtained under alkaline conditions.[1–3]



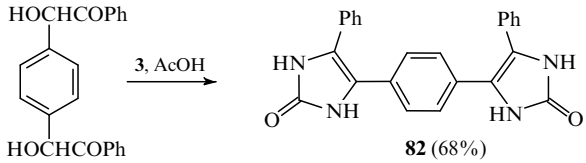
R = H, Alk.

One of the common reactions for the synthesis of imidazolin-2-ones **81** is the cyclisation of acyloins with urea.[40, 80]

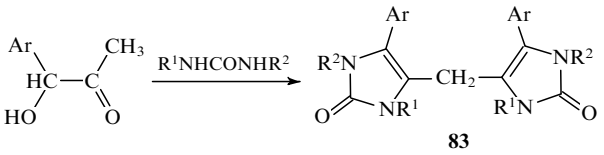


R = Alk, Ar, ArAlk.

Arylenebishydroxyketones react with urea under an argon atmosphere to form arylenebisimidazolinones **82**.[81]



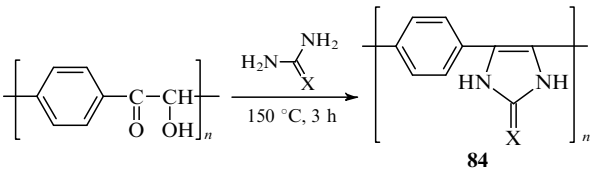
Certain alkylarylacyloins react with urea under the conditions of acid catalysis, affording the methylenebisimidazolinones **83**,[82] which are formed with participation of the activated CH_3 groups.



83

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

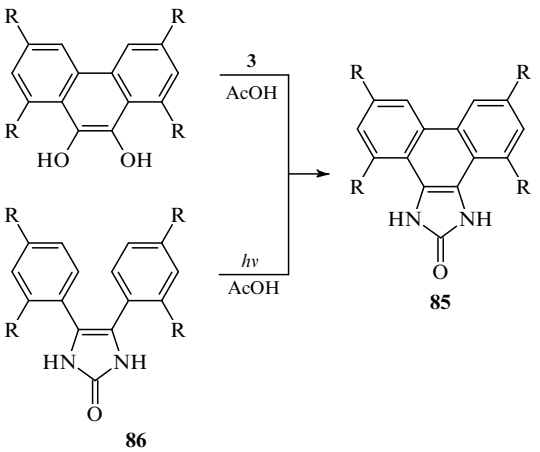
Polyacyloins also react with urea and thiourea, giving rise to polyimidazolinones (thiones) **84**, which are important ingredients of polymeric composite materials.[83]



84

X = O, S; n = 15–10000.

The cyclocondensation of phenanthrene-9,10-diols with urea leads to the phenanthroimidazolinones **85**, the structure of which has been confirmed by specific synthesis — the photolysis of 4,5-diaryl-2-imidazolinones **86** in acetic acid.[84]



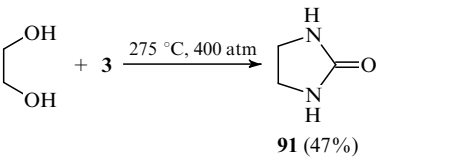
85

86

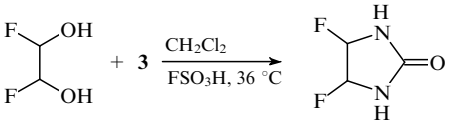
R = H, Me, Cl, Ph.

Aliphatic and alicyclic α-bromo ketones proved to be convenient starting materials for the synthesis of the imidazolin-2-ones **87**–**90**[85–90] (Scheme 3). Imidazolinones of type **88** have also been obtained from α-keto alcohols and urea at comparatively low temperatures (125 °C) in the presence of phosphomolybdic acid.[91] The imidazolinones **87** and **88** are intermediates in the synthesis of biotin.

The imidazolidin-2-ones **91** and **92** are obtained as a rule by the condensation of aliphatic 1,2-diols with urea. Thus the interaction of ethylene glycol with urea under fairly severe conditions affords imidazolidin-2-one **91**.[92]

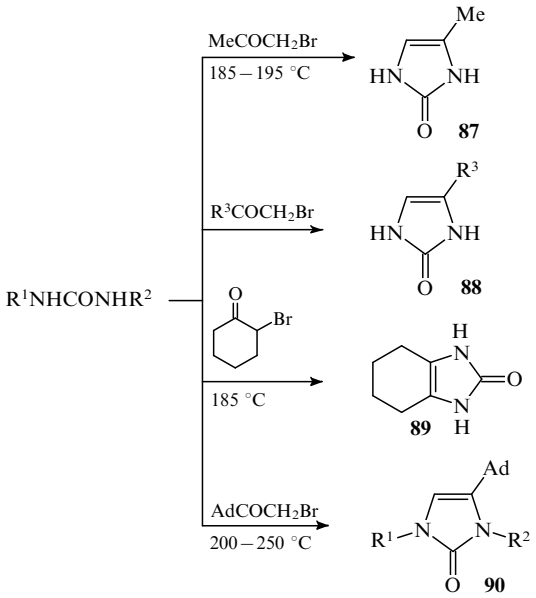


91 (47%)



92

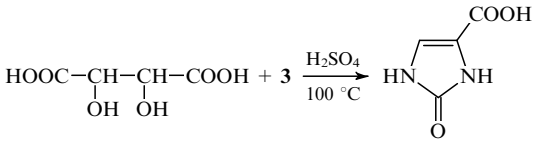
Scheme 3



R^1 = H, Ph, Ac; R^2 = H; $R^3 = C_5H_{11}$; Ad = adamantyl.

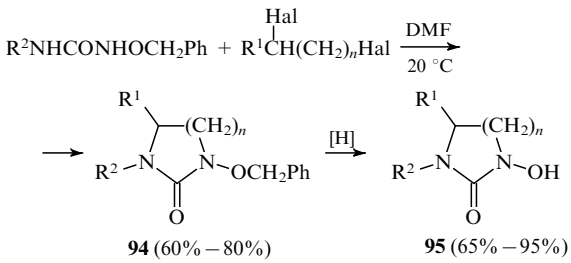
The presence of a fluorine atom in the 1- and 2-positions in the initial ethylene glycol facilitates significantly the formation of 4,5-difluoroimidazolidin-2-one **92**.[93]

The cyclisation reaction between tartaric acid and urea **3** in concentrated sulfuric acid proceeds with participation of only the hydroxy-groups and is completed by the formation of 2-oxoimidazoline-4-carboxylic acid **93**.[94]



93 (51%)

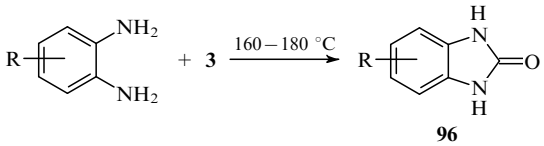
Alkoxyimidazolidin-2-ones **94** (n = 1) are obtained by the alkylation of alkoxyureas with dihaloalkanes in DMF. The hydrogenolysis of compounds **94** ($HCOONH_4$–Pd/C) leads to the corresponding *N*-hydroxyimidazolidin-2-ones **95** (n = 1).[95]



94 (60%–80%) **95** (65%–95%)

R^1 = COOEt, H, CN; R^2 = H, Alk; n = 1, 2.

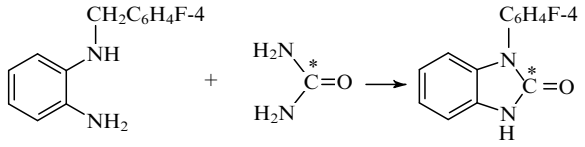
The commonest method of synthesis of benzimidazolin-2-ones **96** is perhaps the cyclocondensation of *o*-phenylenediamines with urea **3**.[96–101]



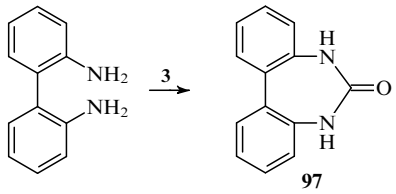
96

R = H, Alk, Ar, Hal, OAlk, COOH, CN.

Heterocyclic 1,2-diamines react similarly with urea.[102] It has been shown that the interaction of *N*-(4-fluorobenzyl)-*o*-phenylenediamine with [^{14}C]urea results in the formation of 2-[^{14}C]-1-(4-fluorophenyl)-2,3-dihydrobenzimidazolin-2-one.[103]



It has been reported [104] that, on refluxing with urea in pentyl alcohol, 2,2′-diaminobiphenyl readily affords dibenzodihydrodi-1,3-azepin-2-one **97**.

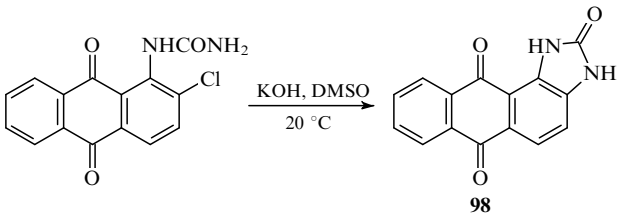


97

Aliphatic 1,2-diamines condense with urea at 200–260 °C in polar solvents.[105–107] At a temperature above 180 °C, urea forms cyclic products also with diamines of the type $RNH(CH_2)_nNHR$ (n = 3, 4).[108]

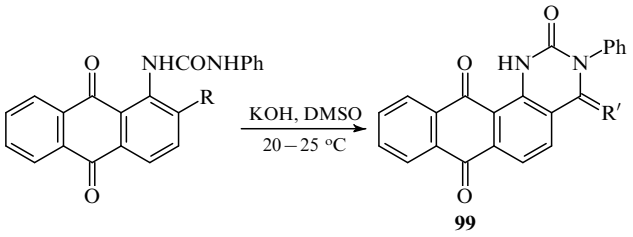
b. Intramolecular cyclisation of ureas

Anthraquinonoimidazolinone **98** has been synthesised by intramolecular substitution of the chlorine atom in a superbasic medium.[109]



98

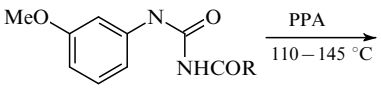
The intramolecular cyclisation of 2-substituted ureidoanthraquinones in a superbasic medium leads to angular condensed heterosystems — derivatives of naphthoquinazoline **99**.[110]

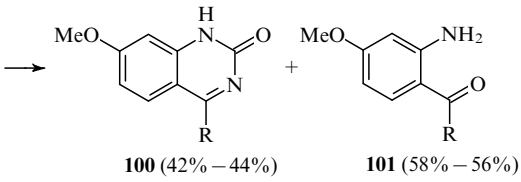


99

R = C≡CPh, COOH; R′ = *Z*-CHPh (14.5%), *E*-CHPh (51%), O (27%).

The cyclisation of *N*-acyl-*N*′-(3-methoxyaryl)ureas in the presence of polyphosphoric acid (PPA) affords the dihydroquinazolinones **100** and their hydrolysis products **101**.[111]

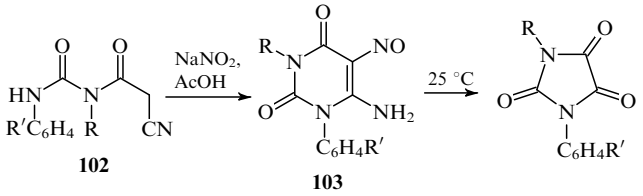




100 (42% – 44%) **101** (58% – 56%)

R = Me, Het.

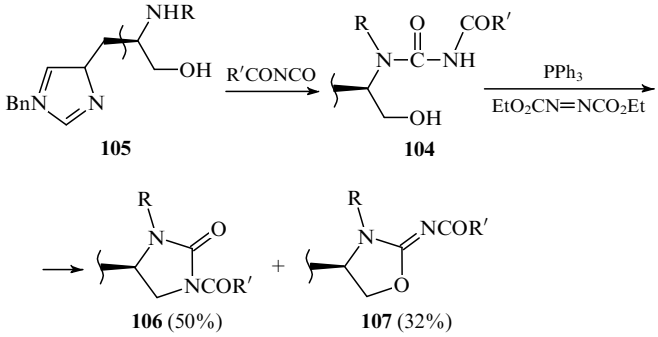
On treatment with sodium nitrite in water in the presence of acetic acid, the cyanoacetylureas **102** are initially converted into the uracil derivatives **103**. However, the latter undergo an unexpected transformation of the pyrimidine heterocycle, whereupon derivatives of parabanic acid are formed.[112] The available literature data on the ways in which heterocycles are transformed [113] do not provide a satisfactory mechanism of this reaction.



102 **103**

R = H, Me; R′ = H, Hal, Me.

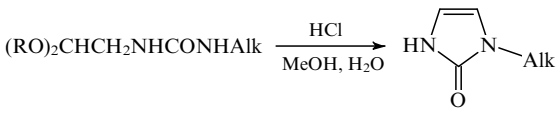
The cyclisation of the aroylureas **104**, obtained from the amino alcohols **105** and aroyl isocyanates, leads to a mixture of heterocyclic compounds — the *O*- and *N*-alkylation products **106** and **107**. An important feature is that the configuration of the asymmetric carbon atom is retained.[114]



105 **104** **106** (50%) **107** (32%)

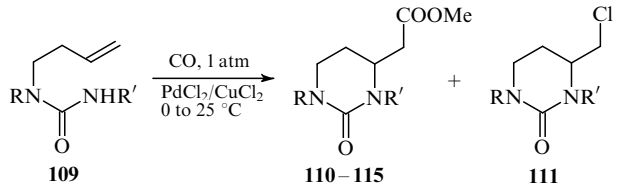
R = Et, Bu^i; R′ = Ph, 4-ClC$_6$H$_4$, 2,4-Cl$_2$C$_6$H$_3$, 2-Cl-4-NO$_2$C$_6$H$_3$.

It has been proposed [115] that the intramolecular cyclisation of the acetals of aldehydoureas in an acid medium be employed in the synthesis of 1-alkyl-4-imidazolin-2-ones **108**.[115]



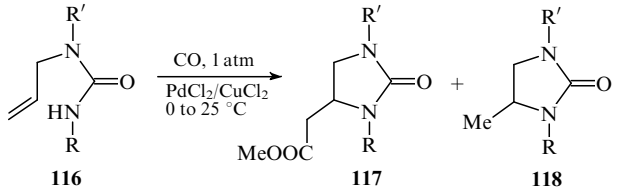
108

On carbonylation in the presence of $PdCl_2/CuCl_2$ in methanol at room temperature and atmospheric CO pressure, the unsaturated urea **109** (R = CH_2Ph, R′ = Me) gives rise to a mixture of perhydrogenated pyrimidinones **110** and **111** (yields 82% and 14% respectively). Only compound **110** is formed at 0 °C. Compounds **112** – **115** have been obtained under similar conditions.[116]

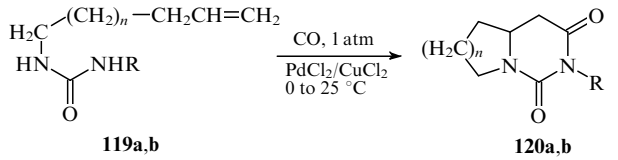


R = CH_2Ph: R′ = Me [**110**, (82%)]; Pr^i, Pr^i [**112**, (84%)];
Pr^i, Me [**113**, (82%)]; Bu^t, Me [**114**, (47%)]; Ph, Me [**115**, (58%)].

The pentylureas **116** afford mixtures of the hydrogenated imidazolidinones **117** and **118** under similar conditions.[116] 1,3-Diazabicyclo[4.3.0]nonane-2,4-diones **120a** and 1,3-diazabicyclo[4.4.0]decane-2 4-diones **120b** are formed under the same conditions from *N*-penten-4-yl- and *N*-hexen-5-yl-ureas (compounds **119a** and **119b**) respectively.[116]

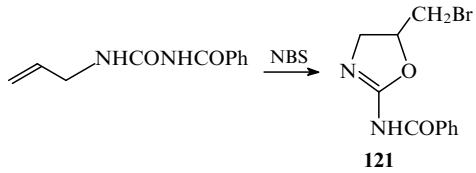


R = Me, Pr^i; R′ = Me, Pr^i, CH_2Ph.

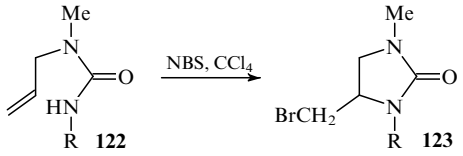


R = Me, Pr^i, CH_2Ph; *n* = 1(**a**); 2(**b**).

The bromocyclisation of allylbenzoylurea on treatment with *N*-bromosuccinimide proceeds with formation of the substituted oxazoline **121**.[56]

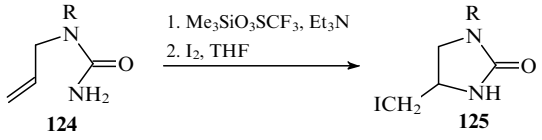


In contrast to this, the halocyclisation of the allylureas **122**, initiated by *N*-bromosuccinimide in CCl_4, leads to the bromomethylimidazolidinones **123**.[58]



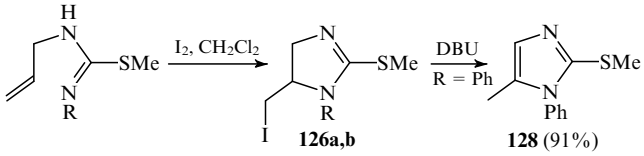
R = Ar, 2-Cl-C_6H_4CO, EtO_2CCH_2.

Preliminary silylation with trimethylsilyl trifluorosulfonate in the presence of NEt_3 in CH_2Cl_2 is necessary for the conversion of the allylureas **124** into the iodoethylimidazolines **125**.[57]

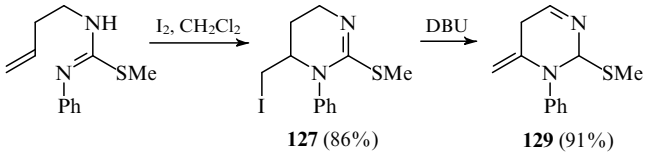


R = Me (83%), $PhCH_2$ (71%).

Imidazoline derivatives **126** or tetrahydropyrimidine derivatives **127** are formed on iodocyclisation of unsaturated isothioureas. After treatment with diazabicycloundecane, they are converted into compounds **128** and **129** respectively.[57]

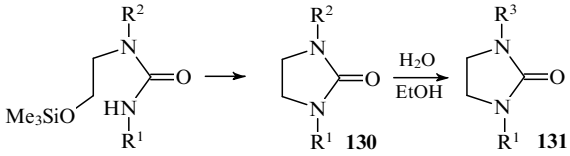


R = Ph [**126a**, (89%)], Ac [**126b**, (77%)].



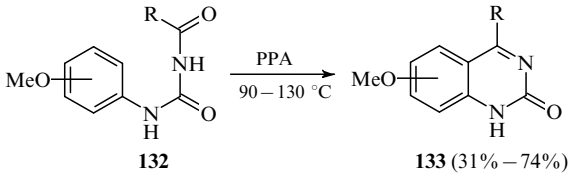
DBU = diazabicycloundecene.

After prolonged storage in the light in the absence of contact with air, intramolecular cyclocondensation of substituted 2-trimethylsilyloxy ethylureas takes place and leads to the imidazolidinones **130**. Their subsequent hydrolysis affords the imidazolidin-2-ones **131**.[117]



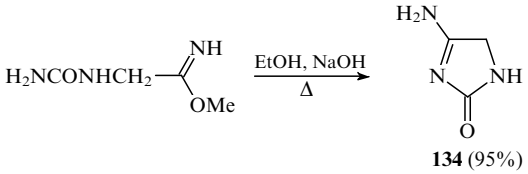
R^1 = Alk, R^2 = Me_3Si, $Me_3SiOCH_2CH_2$, R^3 = H, CH_2CH_2OH.

The heterocyclisation of *N*-acyl-*N*′-arylureas **132** on treatment with polyphosphoric acid leads to 4-substituted quinazolin-2-ones **133**, which are believed to be formed as a result of a reaction of the Bischler–Napieralski type.[118]

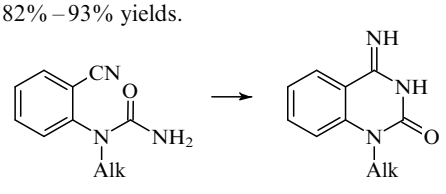


R = Alk, Ph.

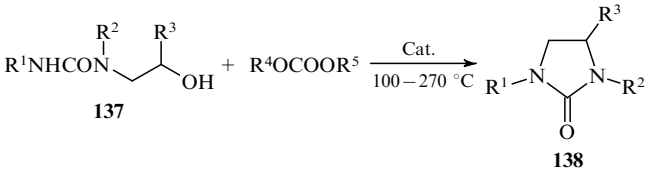
According to patent data,[119] the refluxing of the iminoester of ureidoacetic acid with alkali in aqueous alcohol leads to 4-amino-Δ^3-imidazolin-2-one **134** in a high yield.



It has been established [120] that, on exposure to ultrasound in the presence of baker's yeast, *ortho*-substituted carbamide derivatives of benzonitrile **135** cyclise to the 4-iminoquinazolinones **136** in 82%–93% yields.



The cyclisation reaction between β-hydroxyethyl(propyl)-ureas **137** and carbonic acid esters, catalysed by Group I–IV metal halides, is completed by the formation of substituted imidazolidin-2-ones **138** in yields up to 60%. They are of interest as monomers and comonomers for the manufacture of plastics, coatings, varnishes, and ion-exchange resins.[121]



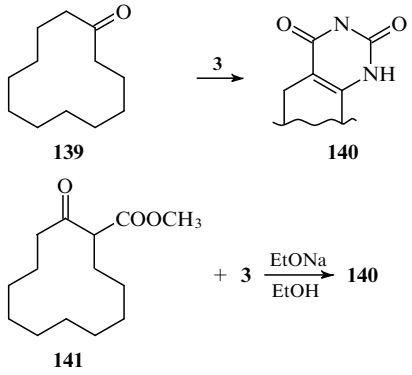
137 **138**

$R^1 = R^2$ = Cl, Br, NO_2, CF_3, Alk(C_1–C_4)O, Ar; R^3 = H, Me; R^4, R^5 = Alk(C_1–C_4);

c. Other methods of synthesis

An erroneous structure was initially attributed to the compound obtained by the condensation of cyclohexanone with urea on refluxing in *o*-xylene.[122] It was later established that[47] it is 5,6,7,8-tetrahydrospiro[cyclohexane-1,2′(1*H*)-quinazoline]-4′(3′*H*)-one. In contrast to cyclohexanone, the high-temperature condensation of cyclododecanone **139** with urea at 280 °C[123] or on refluxing in *o*-xylene in the presence of *p*-TsOH (150 °C, 8 h)[123] leads to the condensed pyrimidine (1*H*,3*H*)-2,4-dione **140**.

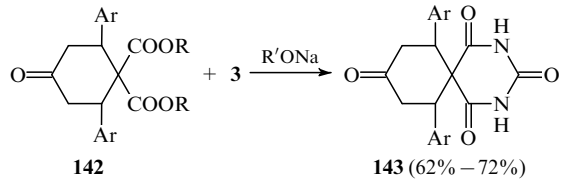
Compound **140** has also been obtained by an independent synthesis from methyl 2-oxocyclododecanecarboxylate **141** and urea in the presence of sodium ethoxide.[123]



139 **140**

141

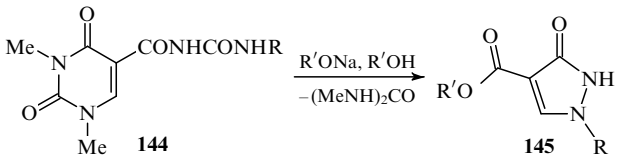
The spiro-compounds **143** have been synthesised in satisfactory yields by the cyclocondensation of the dialkyl esters of 2,6-diaryl-4-oxocyclohexane-1,1-dicarboxylic acids **142** with urea in the presence of sodium alkoxides.[124]



142 **143** (62%–72%)

R = R′ = Me, Et.

A remarkable example of the intramoleclar rearrangement of the uracil derivatives **144** to the pyrazolones **145** has been described.[125] Thus the refluxing of the ureides **144** in EtOH or MeOH in the presence of sodium alkoxides affords the pyrazolones **145** and the symmetrical dimethylurea as a result of the intramolecular rearrangement of the ureides **144** and the attack by the alkoxy-group on the carbonyl C(6) atom.[125]

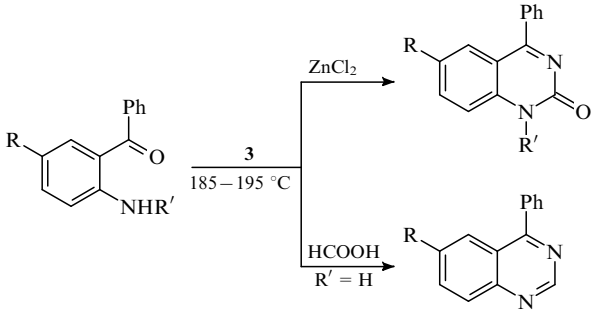


144 **145**

R = H, Me; R′ = Me, Et.

2-Aminobenzophenones are key compounds for the synthesis of tranquilisers of the 1,4-benzodiazepine series. The heterocyclisation reaction between 2-aminobenzophenones and urea **3** leads to quinazoline derivatives.[126–129]

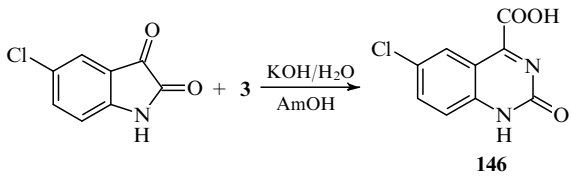
The cyclisation in the presence of $ZnCl_2$ affords 1-R′-6-R-4-phenylquinazolin-2-ones,[128–130] while 6-R-4-phenylquinazolines are formed in the presence of formic acid.[131, 132]



R = H, Cl; R′ = H, Me.

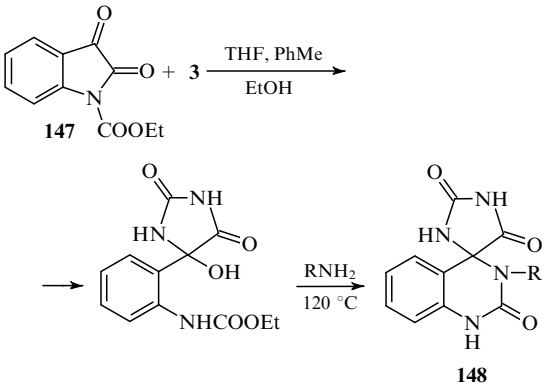
It has been shown that *N*-allyl-*N*-nitrosourea is converted into pyrazole in 18% yield *via* the intermediate vinyldiazomethane.[125]

6-Chloro-2-quinazolone-4-carboxylic acid **146** has been synthesised by condensing 5-chloroisatin with urea in 1-pentanol in the presence of aqueous KOH.[131]



146

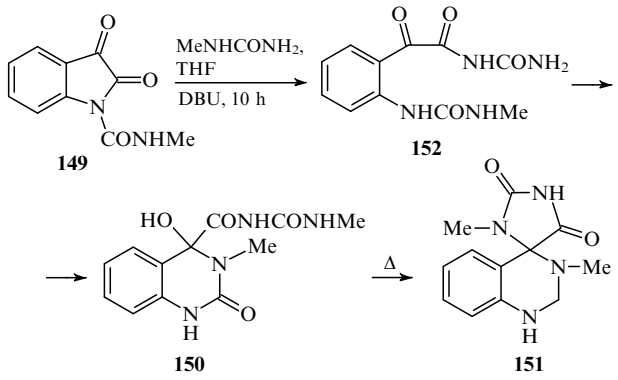
It has been established that, on heating in a sealed tube with ammonia, hydrazine, or hydroxylamine, *N*-ethoxycarbonylisatin **147** and urea afford spiro[imidazolidine-4,4′(1*H*)-quinazoline]-2,2′,5(3*H*) triones **148** after 4 h at 120 °C.[132]



147 **148**

R [yield (%)]: H(59), NH_2(57), OH(15).

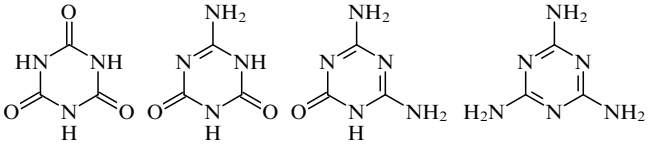
On interaction with methylurea in boiling THF, *N*-methylcarbamoylisatin **149** recyclises to the ureidoquinazolin-2-one derivative **150** in 29% yield after 5 h in the presence of diazabicycloundecene. On refluxing in 1,2-dichlorobenzene, compound **150** is converted into the spiro-compound **151** in 97% yield.[132]



According to the data of Yamagishi *et al.*,[133] the ureidoquinazolinone **150** is formed from *N*-methylcarbamoylisatin **149** and methylurea *via* the acyclic intermediate **152**.

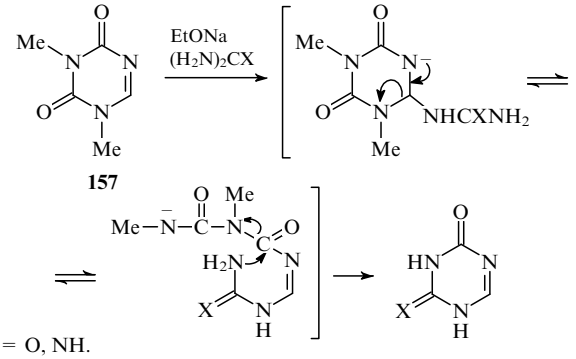
3. Syntheses of heterocycles containing three nitrogen atoms

Cyanuric acid — 1,3,5-triazine-2,4,6-trione **153** — is perhaps the main representative of azaheterocycles containing three nitrogen atoms. As a consequence of its unique properties, it has found application in various branches of industry.[134] Cyanuric acid is obtained mainly by the pyrolysis of urea in organic solvents in a fluidised bed on the surface of metals.[134] However, the pyrolysis affords, together with cyanuric acid, also related triazines — ammelide **154**, ammeline **155**, and melamine **156** — the products of the amination of cyanuric acid which are of independent practical interest.[134, 135]

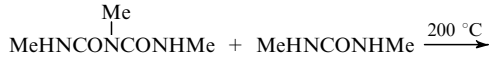


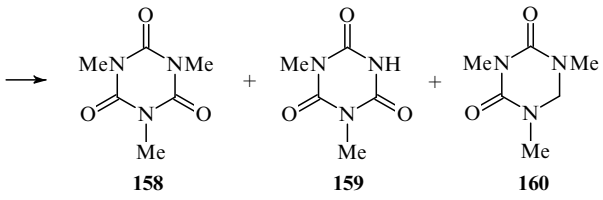
All these heterocycles are products of the cyclotrimerisation of isocyanic acid and/or cyanamide.

The recyclisation–cyclisation of 1,3-dimethyl-1,3,5-triazine-2,4-dione **157** on treatment with urea or guanidine in DMF in the presence of bases has been observed recently.[136]

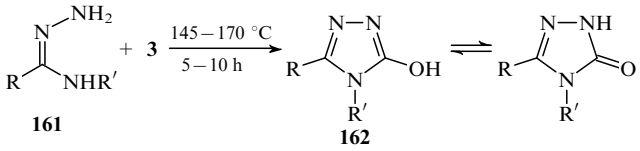


The interaction of 1,3,5-trimethylbiuret with 1,3-dimethylurea in chloroform at 200 °C leads to a mixture of the triazinones **158**–**160**.[137]





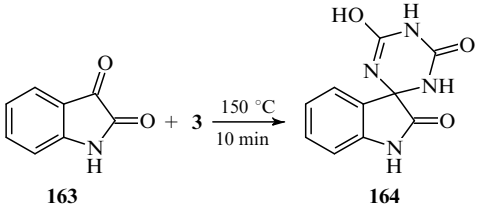
Substituted amidrazones **161** react with urea to form 4,5-disubstituted 3-hydroxy-1,2,4-triazoles **162** in 54%–78% yields.[138]



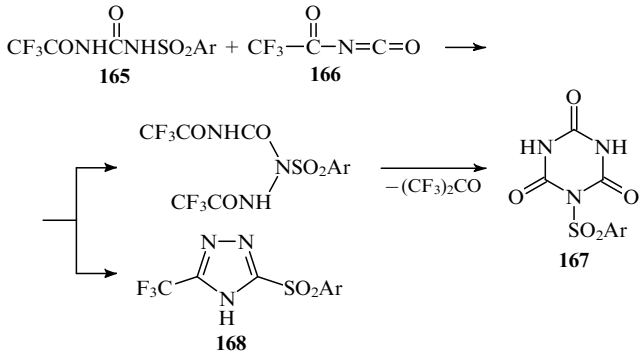
R = Ph,  ; R′ = Ar.

3-Hydroxy-*sym*-triazolo[4,3-*a*]pyridine and 3-hydroxy-*sym*-triazolo[4,3-*a*]phthalazine are formed on interaction with 2-hydrazinopyridine[139] or 1-hydrazino-phthalazine[140] respectively with urea.

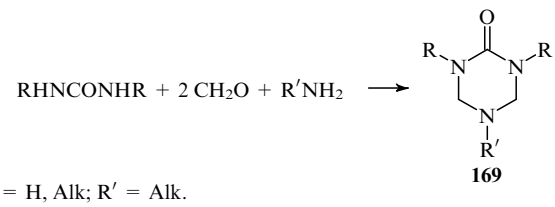
The reaction of isatin **163** with urea is rapid and leads to the formation of 2-oxoindolinyl-3-spiro-2′-(6′-hydroxy-4′-oxo-2′,3′,4′,5′-tetrahydro-*sym*-triazine) **164** in 34% yield.[141]



The presence of a mobile hydrogen atom in *N*-acyl-*N*′-arenesulfonylureas **165** and their tendency to undergo tautomeric transformations in reactions with acyl isocyanates **166** promotes the formation of the *sym*-triazine (compounds **167**)[58–61] or triazole (compounds **168**) rings.[142]

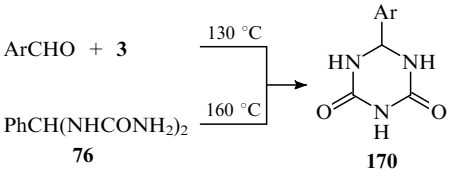


Urea or its mono- and *sym*-di-substituted derivatives react with 2 equivalents of formaldehyde and 1 equivalent of a primary amine to form 5-alkyl-2-oxotetrahydro-1,3,5-triazines **169**.[143] Glycylglycine enters into a similar reaction.[144]

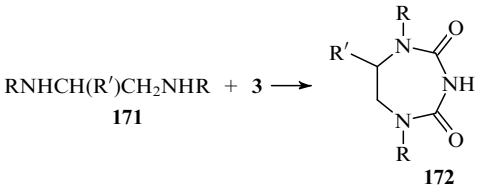


R = H, Alk; R′ = Alk.

Perhydro-4-aryl-1,3,5-triazine-2,4-diones **170** can be synthesised either by the direct condensation of the corresponding substituted benzaldehydes with urea [145, 146] or by the intermolecular cyclisation of benzylidenebisurea **76** in DMSO.[147]



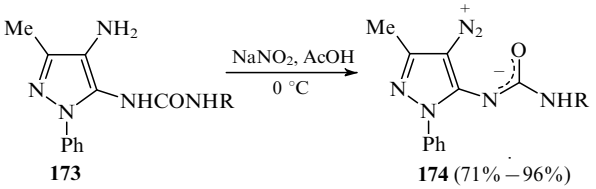
2-Aryl(heteroaryl)-1,2,3-triazoles, which have the properties of optical bleaching agents, are synthesised by the interaction of compounds of the type A[NHN=C(Alk, Ar)C=NOH]$_n$ (where A = aromatic or heterocyclic residue) with an excess of urea in water.[148] According to patent data,[149] the hydroxyalkyl derivatives of 1,3,5-triazacycloheptane-2,4-dione **172** have been obtained by the reaction of the diamines **171** with urea **3** or biuret at 100–150 °C in DMSO or DMF.



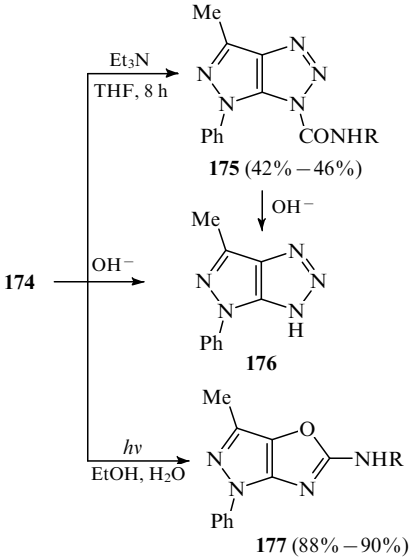
R = CH_2CH_2OH; R′ = H, Alk.

4-Diazopyrazoles **173**, obtained by the diazotisation of *N*-alkyl-*N*′-(4-amino-5-pyrazolyl)ureas **174**, proved to be convenient synthons for the construction of various heteocyclic compounds of types **175**–**177** [150] (Scheme 4).

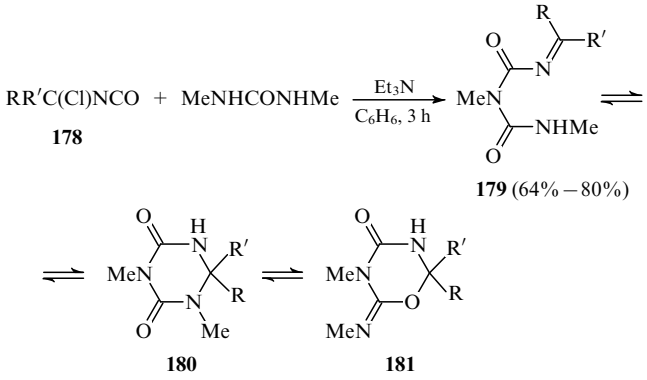
Scheme 4



R = Me, CH_2Ph.



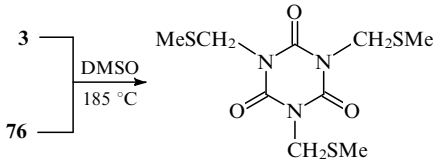
The interaction of 1-chloroisocyanates **178** with 1,3-dimethylurea involves *N*-acylation with formation of the corresponding *N*-alkylideneaminocarbonylurea **179**.[151]

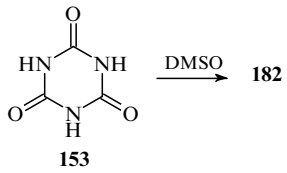


R = H, CF_3; R′ = Ar, P(O)(OEt)$_2$.

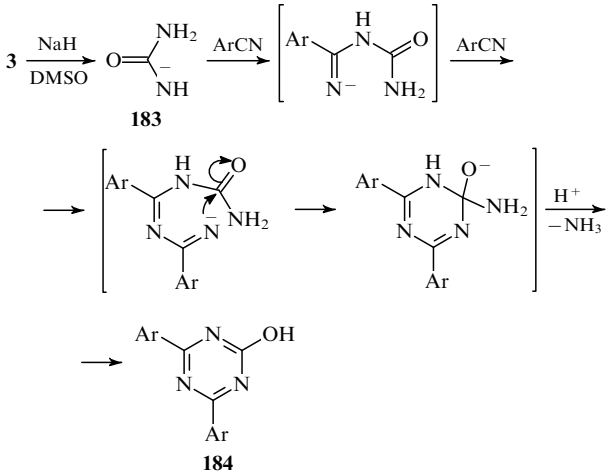
Analysis of NMR spectroscopic data in polar solvents led to the observation that *N*-alkylideneureas **179** contain up to 13% of compounds **180** and **181**, formed as a result of intramolecular cyclisation.

The high-temperature reaction of ureas **3** or benzylidenebisurea **76** with DMSO constitutes a single-stage method of synthesis of 1,3,5-tris(methylthiomethyl)-1,3,5-triazine-2,4,6-trione **182**.[152] The reaction of cyanuric acid **153** with DMSO also leads to compound **182**. On this basis, it has been concluded that cyanuric acid is an intermediate in the synthesis of the triazine **182** from ureas.

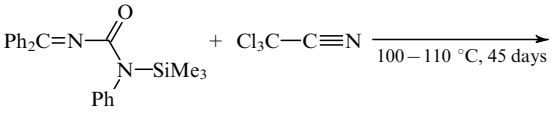




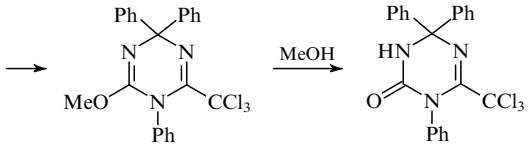
The interaction of the anion **183**, obtained from urea **3** by treatment with NaH in DMSO, with aromatic nitriles [123] leads to 4,6-diaryl-2-hydroxy-*sym*-triazines **184**. It has been suggested that the reaction is a two-stage process.



As a result of its reaction with trichloroacetonitrile in benzene in a sealed tube and subsequent treatment of the reaction product **186** with methanol, the arylideneurea derivative **185** affords the *sym*-triazinone **187**.[154]



185

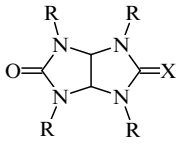


186 **187**

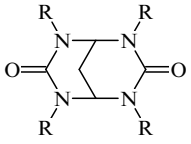
III. Methods of synthesis of bicyclic azaheterocycles

Bicyclic bisureas (BBU) have been known since the end of the past century. The principal methods of their synthesis, described in the literature up to 1972, have been surveyed.[155] By virtue of the valuable properties of the BBU, the methods of their synthesis using ureas are being constantly improved.

The most successful classification of the BBU, represented by structures of the type **188**–**191** which differ in the size of the rings and the ways in which they are joined together, has been proposed in Ref. 156.

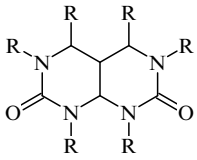


188

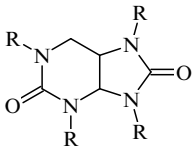


189

X = O, S.



190



191

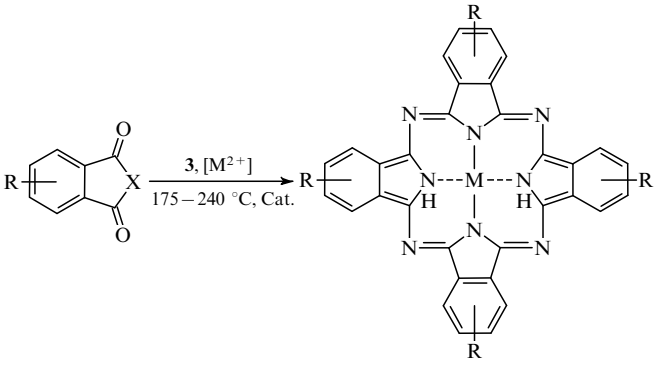
Since fundamentally new approaches to the synthesis of the BBU have not been developed in recent years, we shall confine ourselves to reactions by means of which the BBU are obtained. Furthermore, we shall present data which appeared in the literature after the publication of the review in Ref. 155.

The BBU of the bicyclooctane series **188** are synthesised by the reactions of 1,2-diketones,[77,78,157–163] α-hydroxy ketone,[81,82] α-ketomonooximes, and α-isonitroso ketones[164] with ureas, predominantly under the conditions of acid catalysis. The type **188** BBU can be obtained stepwise. 4,5-Dihydroxyimidazolidin-2-ones are synthesised initially from the corresponding 1,2-bifunctional compounds and ureas and are then cyclocondensed with ureas and thioureas to compounds **188**.[71] An advantage of the stepwise synthesis of the BBU is that this approach makes it possible to obtain BBU with an asymmetric structure. The BBU of the bicyclononane series **189** are synthesied by the reactions of 1,3-dicarbonyl compounds or their analogues with ureas.[155,165–167] The BBU of the bicyclodecane series **190** and compounds of type **191** are as a rule synthesised from ureidopyrimidines prepared beforehand[155,168] or by the interaction of the latter with aldehydes.

The kinetics of the reactions of carbonyl compounds with ureas have been investigated and the mechanisms of the formation of the BBU have been proposed in a series of studies.[77,78,158,159,161–163,167] The main requirement for the successful synthesis of the BBU **188**–**191** is the creation of conditions under which urea would not decompose.

IV. Methods of synthesis of phthalocyanines, diazepines, and diazocines

The decomposition of urea with elimination of ammonia at high temperatures has been used successfully in the amination of various organic substrates. One of the main synthetic applications of urea as an aminating agent is the preparation of phthalo- and naphthalo-cyanines. Phthalocyanines **192** are obtained from phthalic acids.[168] However, the main synthesis is from their anhydrides and imides[168–172] or from phthalodinitrile[173] on interaction with urea **3** in the melt in the presence of transition metal (Cu;[168–171,174] Ni or Co[172,173]) compounds and a catalyst. The synthesis is sometimes carried out in high-boiling solvents.



192

R = H, NO_2, Alk, Ar, NH_2;
X = NH, O; M^{2+} = Cu, Ni, Co.

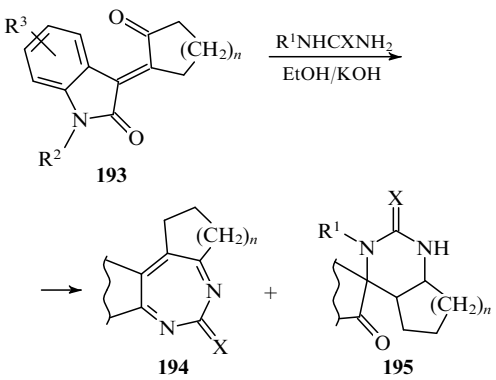
Molybdenum compounds and more rarely titanium or zirconium salts are used as catalysts for the synthesis of phthalocyanines.[168]

Substituted phthalocyanines and their complexes with vanadium oxide are obtained in high yields by the high-temperature reaction of 4,5-dichloro-3,6-di(phenylthio)phthalic anhydride with urea in the presence of ammonium molybdate and VOCl in trichlorobenzene on heating.[175] Naphthalocyanines are synthesised similarly from derivatives of naphthalene-2,3-dicarboxylic acids and urea. The latter is used as the aminating agent.[172,176–178] Macrocyclic phthalocyanines and naphthalocyanines have found wide applications as optical, recording, and photosensitive materials.

The polymeric platinum-phthalocyanine is obtained by the reaction of pyromellitonitrile, $PtCl_2$, and urea and is used as the catalyst in the formation of indole from *N*-ethylaniline.[179]

Tetrafluorinated[180] or tetrasulfonated[181] phthalocyanines have been obtained by the reaction of the corresponding anhydrides or ammonium salts with urea in the presence of suitable metal salts.

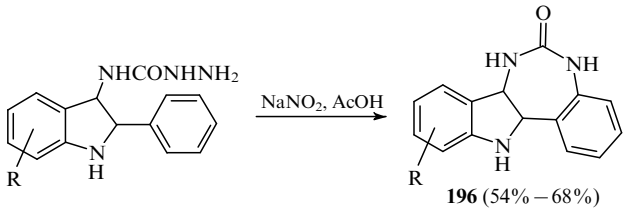
It has been shown in a number of studies[182–184] that urea can be used in the synthesis of benzodiazepine derivatives, which are of independent interest for pharmacology. Thus the interaction of 3-(2-oxocycloalkylidene)indolin-2-ones **193** with urea or thiourea in an alcoholic KOH solution leads to a mixture of reaction products: a tetracyclic system comprising indolodiazepinones (thiones) **194** and spiro-2-indolinones **195**. The yields of the reaction products were 30%–35% for **194** and 40%–50% for **195** respectively.[182]



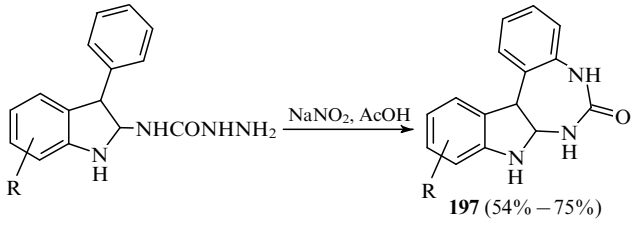
193 **194** **195**

R^1 = H, Ar; R^2 = H, Me, Ac; R^3 = H, F, CF_3;
X = O, S; *n* = 1, 2.

Cyclic ureas of the indolo[3,2-*d*]benzo[1,3]diazepin-2-one **196** and indolo-[2,3-*d*]benzo[1,3]diazepin-2-one **197** series are formed when 2-phenylindolyl-3-semicarbazides or 3-phenylindolyl-2-semicarbazides are treated with sodium nitrite in acetic acid.[183]



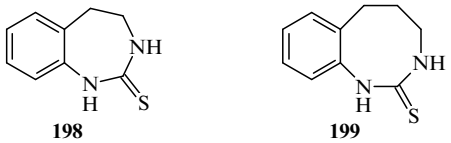
196 (54% – 68%)



197 (54% – 75%)

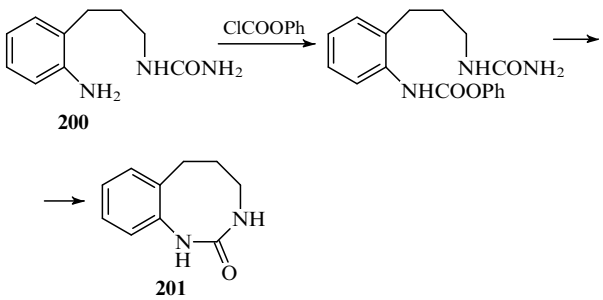
R = 5-Me, 5-Cl, H, 6,7-CH=CHCH=CH.

Examples of the formation of the diazepine and diazocine rings from ureas and 1,4- or 1,5-diamines respectively have been published.[184] For example, 1,3,4,5-tetrahydro-2*H*-benzo-1,3-diazepine-2-thione **198** and 1,2,3,4,5,6-hexahydrobenzo-1,3-diazocine-2-thione **199** have been synthesised from the corresponding diamines and thiourea.



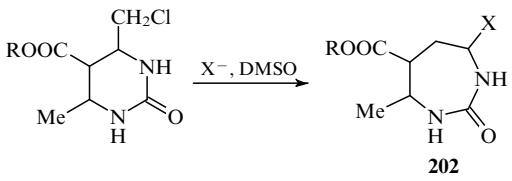
198 **199**

Benzo-1,3-diazocin-2-one **201** is synthesised from 1,4- and 1,5-diamines *via* a series of intermediate stages leading to the N-substituted urea **200**.[184]



200 **201**

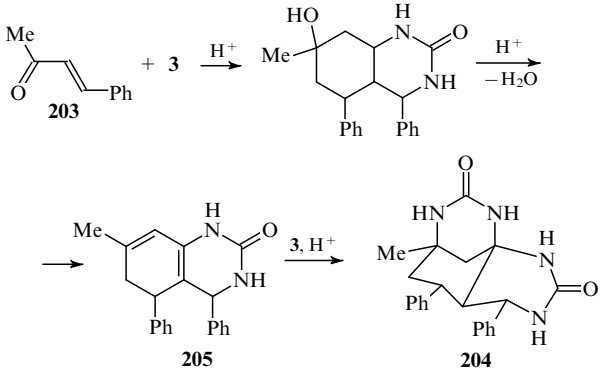
On treatment with nucleophiles, 4-chloromethyltetrahydropyrimidin-2-ones undergo ring expansion, which leads to the 1,3-diazepinone derivatives **202**.[185]



202

R = Me, Et; X = CN, SH, OEt, OMe, SO_2H, H, NR_2.

The interaction of 4-phenylbut-3-en-2-one **203** with urea in ethanol in the presence of an acid leads to the pyrimido[4,5-*d*]-1,3-diazocinedione **204** after 24 h at 50 °C.[186]



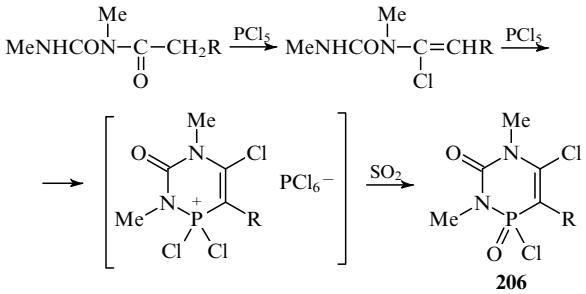
203 **205** **204**

It has been suggested that the quinazolinone **205** is an intermediate in the synthesis of the diazocinedione **204**. Its formation may be represented as a synchronous reaction of two molecules of the phenylbutenone **203** with urea.

V. Synthesis of azaheterocycles containing other elements

1. Phosphorus-containing heterocycles

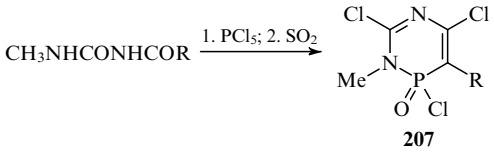
The presence of a series of nucleophilic reaction centres in the carbamide fragment of *N*-acylureas promotes the heterocyclisation of the latter on treatment with phosphorylating agents. Thus the interaction of *N*,*N*′-dimethylacylureas with PCl_5 in proportions of 1 : 5 results in the formation of diazaphosphorinones, which are converted *in situ*, on treatment with SO_2, into 4,6-dichloro-1,3-dimethyl-5-R-2,4-dioxo-1,3,4-diazaphosphorines **206**.[187]



206

R = H, Me.

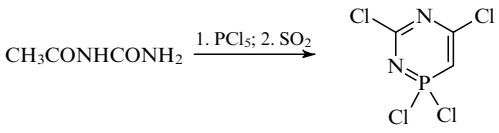
In contrast to dimethylacylureas, the reaction of monomethylacylureas with phosphorus pentachloride is completed mainly by the formation of a compound of the type $[Cl_3P=NC(Cl)=CHPCl_3]^+PCl_6^-$ and a small amount (8.5%) of 2,2,4,6-tetrachloro-1-methyl-1,2-dihydro-1,5,2-diazaphosphorinonium hexachlorophosphorate. On treatment with SO_2, the latter is readily converted into 2,4,6-trichloro-3-methyl-4-oxo-3,4-dihydro-1,3,4-diazaphosphorine **207**.[188]



207

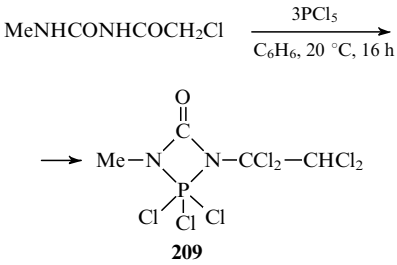
R = H, Me.

It has been shown [189–191] that the phosphorylation of *N*-acetylurea with a fivefold excess of PCl_5 proceeds with participation of the acetyl and free amino-groups with formation of 2,4,4,6-tetrachloro-1,3,4-diazaphosphorine **208** in a satisfactory yield.



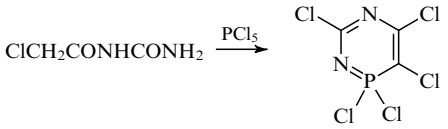
208 (60.5%)

Treatment of *N*-chloroacetyl-*N′*-methylurea with phosphorus pentachloride results in the formation of the substituted 1,3,2-diazaphosphetidin-4-one **209**.[192, 193]



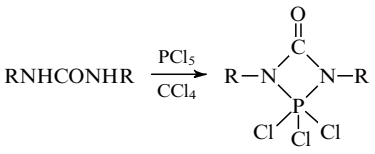
209

On the other hand, heating of chloroacetylurea with PCl_5 leads to 2,4,4,5,6-pentachloro-1,3,4-diazaphosphorine **210**.[194]



210

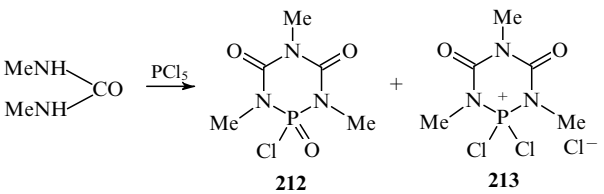
1,3-Dialkyl(alkylaryl)-2,2,2-trichloro-1,3,2-diazaphosphetidin-4-ones **211** are obtained by the reaction of equimolar amounts of PCl_5 and *N*,*N′*-dialkyl-(alkylaryl)ureas.[195] When an excess of PCl_5 is employed, the carbonyl group is chlorinated.[196]



211 (45% – 87%)

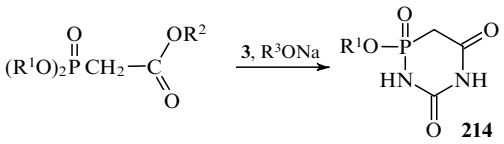
R = Alk (C_1-C_4).

The 1,3,5,2-triazaphosphorines **212** and **213** are obtained by the interaction of PCl_5 with *sym*-dimethylurea.[197]



212 **213**

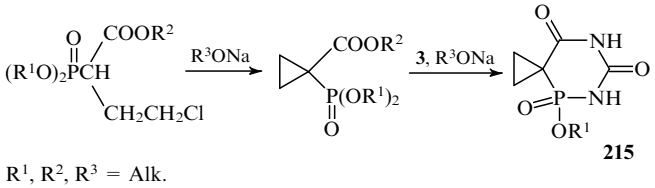
The phosphorus analogues of barbituric acid **214** are formed on condensation of phosphonoacetic acid esters with urea **3** in the presence of sodium alkoxide.[198]



214

R^1, R^2, R^3 = Alk.

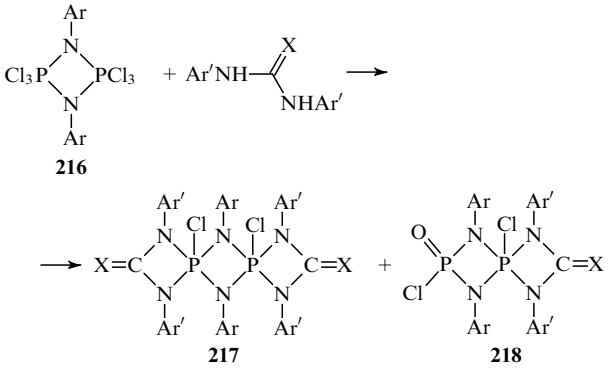
The condensation of 4-chloro-2-dialkoxyphosphorylbutyric acid esters with urea in the presence of sodium alkoxides (1 : 2) leads to spirocyclopropanediazaphosphorinones **215** *via* intermediate cyclopropane derivatives.[199]



215

R^1, R^2, R^3 = Alk.

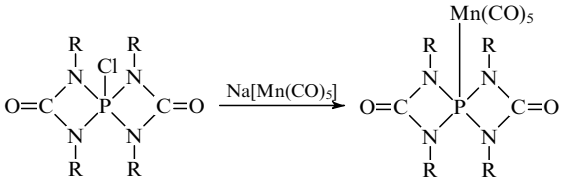
Aryl- and *sym*-diaryl-ureas and -thioureas readily afford the spiro-compounds **217** and **218** after 30 min on interaction with hexachlorodiazaphosphetidine **216** in acetonitrile.[199]



216 **217** **218**

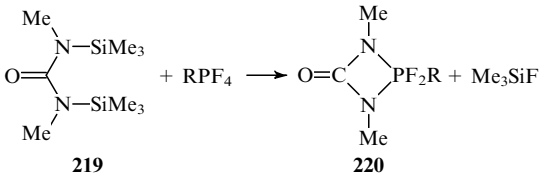
X = O, S.

It has been shown [200] that the chlorine atom in compounds of this type is substituted by pentacarbonylmanganese. The reaction is carried out under an inert atmosphere.



R = Alk, Ar.

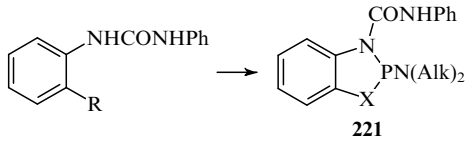
Treatment of symmetrical dimethylsilylureas **219** with alkyl or aryl-fluorophosphanes results in cyclisation with the cleavage of the Si–C bond and the formation of the fluorophosphadiazetinones **220**.[201]



219 **220**

R = Alk, Ar.

The condensation of *o*-amino- or *o*-hydroxy-diphenylureas with tris(dialkylamino)phosphine afforded a series of the corresponding substituted 1,3,2-oxaza- or diaza-benzophospholenes **221**.[202]

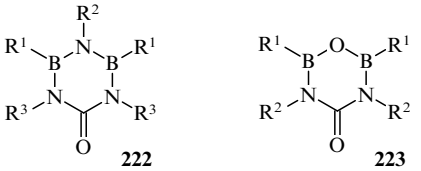


221

R = NH_2, OH; X = O, $NP(NAlk_2)_2$.

2. Boron-containing heterocycles

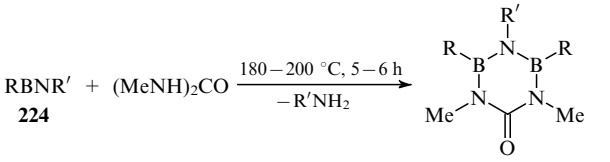
On heating with N-substituted ureas, haloorganylboranes give rise to heterocycles of the type **222** and **223**.[203–205]



222 **223**

R^1, R^2, R^3 = Alk.

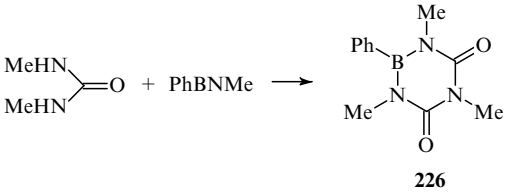
The reaction of the borazines **224** with dimethylurea results in the formation of 1,3,5-triaza-2,4-diboracyclohexan-6-ones **225**.[206]



224 **225** (55%–65%)

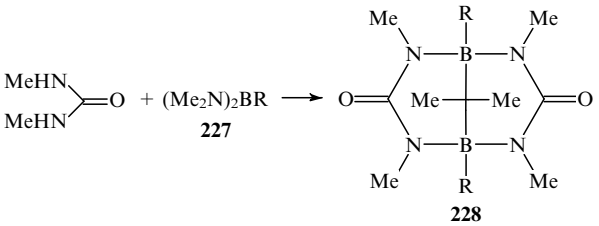
R, R′ = Alk.

The interaction of dimethylurea with borazine yields triazaboracyclohexane-4,6-dione **226** after 10 min.[206] It has been shown that the reaction proceeds *via* the intermediate formation of *N*,*N*′,*N*″-trimethylbiuret.



226

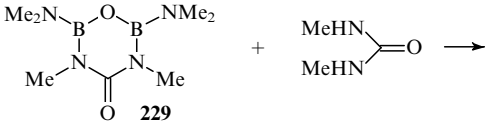
Refluxing of dimethylurea with the borazines **227** in toluene leads to the bicyclic borazinones **228** after 9–10 h.[206]



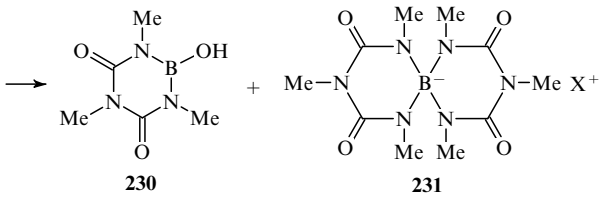
227 **228**

R = Alk, Ph.

The interaction of compound **229** with dimethylurea is used to synthesise the corresponding 1,3,5-triaza-2-boracyclohexane-4,6-diones **230** and a mixture of the ammonium salts of the spirane borates **231**.[207]



229

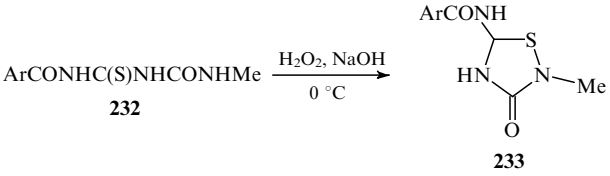


230 **231**

X = Me_2NH_2, MeNH.

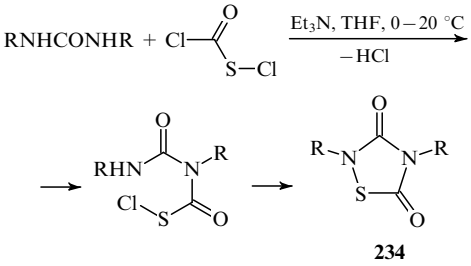
3. Sulfur-containing heterocycles

Aroylthiobiurets **232**, which readily undergo oxidative cyclisation to 5-aroylamino-2-methyl-(2*H*)-1,2,4-thiadiazol-3-ones **233** (yield 31%–85%), have been obtained by the interaction of aroyl isothiocyanates with *N*-methylurea.[208]



232 **233**

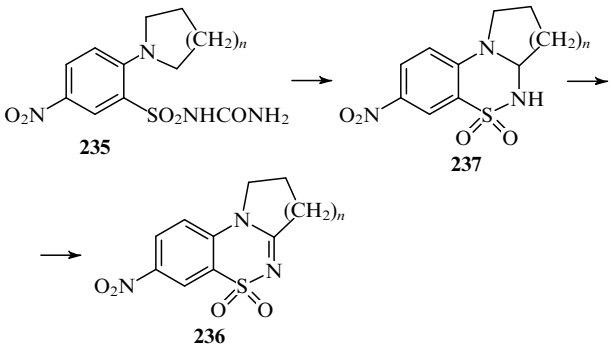
Preparative methods of synthesis have been developed[209] for thiadiazolediones **234** on the basis of the reaction of chlorocarbonylsulfenyl chloride with ureas.



234

R = Me, $MeOCH_2$, cyclo-C_6H_{11}, Ar.

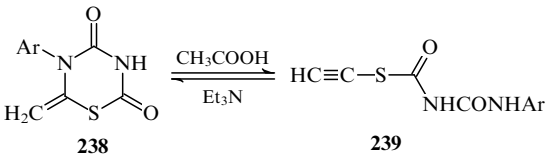
It has been established[210] that, on treatment with a 1:1 mixture of HgO and the disodium salt of ethylenediaminetetraacetic acid, aryl-substituted benzenesulfonylureas **235** cyclise to the sulfonylamidines **236** *via* a stage involving the formation of the sulfonylaminals **237**.



235 **237** **236**

n = 1–3.

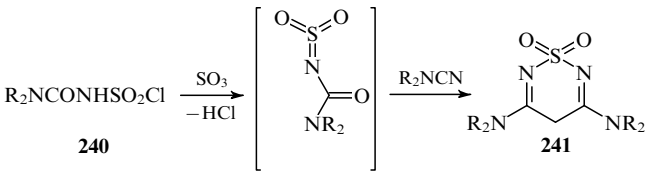
On treatment with catalytic amounts of HCl or CF_3COOH, the thiadiazinediones **238** are capable of undergoing reversible ring cleavage to ethynylthiocarbonylureas **239**. Subsequent treatment of the resulting solutions with an organic base is accompanied by complete displacement of the equilibrium towards the cyclic form **238**.[211]



238 **239**

According to Vovk,[211] the transformation **238** ⇄ **239** is an example of a new type of ring–chain enamidine tautomerism.

The interaction of chlorosulfonylureas **240** with sulfur trioxide and cyanamides entails the formation of 1,4,3,5-oxathiadiazine 4,4-dioxides **241**.[212, 213]

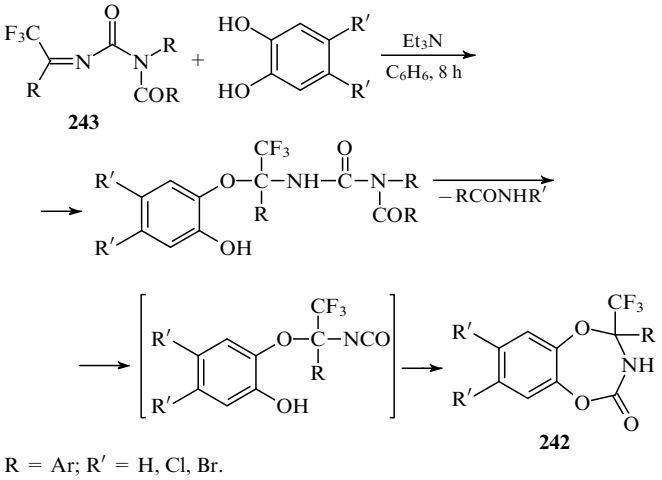


240 **241**

R = H, Alk.

4. Oxygen-containing heterocycles

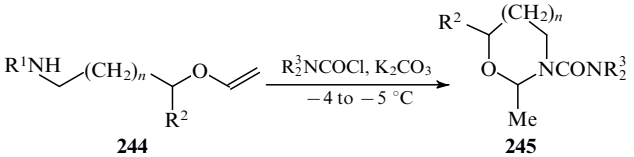
We examined the methods of synthesis of oxazole derivatives using ureas in the previous Sections of this review. The methods of synthesis of compounds with a larger ring size are described here. Thus a series of 1,5,3-benzodioxazepinones **242** have been synthesised in 64%–82% yields by refluxing *N*-alkylidene-*N*′-acylureas **243** with catechol and its derivatives.[214]



243 **242**

R = Ar; R′ = H, Cl, Br.

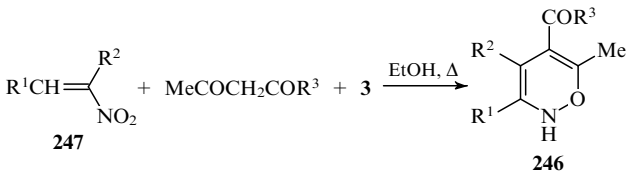
The vinyl ethers of the aminoalcohols **244** give rise to the cyclic carbamides **245** on treatment with *N*,*N*′-dialkylcarbamoyl chlorides in the presence of potassium carbonate and in the absence of steric hindrance to cyclisation.[215]



244 **245**

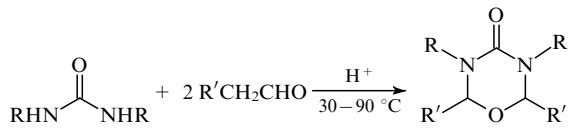
R^1, R^2 = H, Me, Bu, CH_2Ph, cyclo-C_6H_{11};
R^3 = Me, Et, Bu, $C_{12}H_{25}$, $C_{18}H_{37}$;
n = 0, 1.

The substituted 1,2-oxazines **246** have been obtained by a three-component reaction of nitroalkenes **247** with 1,3-dicarbonyl compounds and urea **3**.[216]



247 **246**

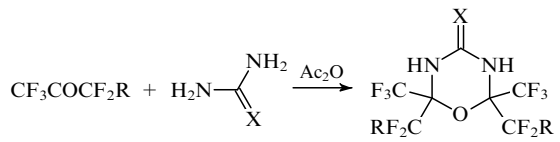
The interaction of unsubstituted urea and of its 1,3-disubstituted derivatives with aldehydes in the presence of acid catalysts results in the formation of 4-oxotetrahydro-1,3,5-oxadiazines **248**.[217, 218]



248

R = H, Alk; R′ = Alk, Ar.

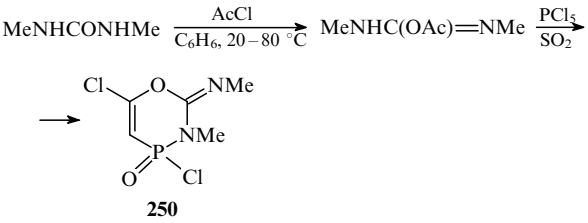
The stable tetrahydro-1,3,5-oxadiazines **249** have been obtained by condensing ureas (thioureas) with polyfluoro ketones in acetic anhydride.[219]



249 (48%–77%)

R = F, NO_2; X = O, S.

4,6-Dichloro-2-(*N*-methylimino)-3-methyl-4-oxo-1,3,4-oxazaphosphorine **250** has been synthesised by acetylating dimethylureas and subsequent treatment of the intermediate with PCl_5 and SO_2.[220]



250

VI. Conclusion

The data presented demonstrate the extensive possibilities for the employment of ureas and related compounds in the synthesis of azaheterocycles with a wide variety of structures — oxazoles, imidazoles, pyridines, phthalocyanines, triazines, and many others. The advances in the practical application of the compounds obtained using ureas, particularly in medicine and biochemistry, are so numerous that they require an independent survey.

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