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Recyclisation Reactions of Heterocyclic Compounds Involving Hydrazine and Its Substituted Derivatives

O.P.Shvaika and V.N.Artemov

In the review an attempt is made for the first time to give a systematic account of the available literature data for the recyclisation reactions of heterocyclic compounds under the influence of two-centre nucleophilic agents-hydrazine and its derivatives. The recyclisation reactions are classified taking into account the capacity of heterocycles to undergo such reactions as a function of the structure and the distribution in the heterocyclic compounds of reaction centres determining the mode of recyclisation. Particular attention has been devoted to heterocyclic rearrangements involving the hydrazine moiety of the molecule. The mechanisms of the recyclisation processes are discussed. The importance of these reactions in organic synthesis has been demonstrated.
The bibliography includes 255 references.

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I. INTRODUCTION

The recyclisation reactions of heterocyclic compounds involve a rearrangement of the heterocyclic skeleton in which the ring heteroatom is replaced and the heterocyclic nucleus is contracted or expanded or undergoes isomerisation. From the theoretical point of view, these reactions are complex transformations involving ring opening and ring closure. Nevertheless for preparative purposes they are single-stage processes. In practice, recyclisation reactions can yield compounds which are frequently difficult to obtain in other ways and allow the transformation of one ring into another in complex molecules, giving rise thereby to a powerful and discriminating synthetic procedure. In their analytical aspect, as a method for the identification of heterocycles, such reactions have been used in biological chemistry.

Recyclisation reactions are a result of the interaction between heterocyclic compounds and other chemical agents or are a consequence of a rearrangement under the influence of temperature, light, or catalysis by acids or bases. Nucleophilic, electrophilic, and dipolar substances can serve as the chemical agents. A number of reviews have been devoted to the transformations of rings under the influence of dipolar agents[1]. The recyclisation reactions under the influence of electrophilic agents are characteristic only of specific heterocyclic systems. However, one frequently encounters ring rearrangements under the influence of nucleophilic agents. The latter must always be binucleophilic. This is because the ring rearrangement—its opening and reclosure—always requires the participation of two reaction centres in the heterocyclic molecule with which the binucleophilic agent interacts. The binucleophilic nature of the substance involved in recyclisation reactions can concern only one or two of its atoms. In the first case we are dealing with one-centre nucleophilic agents such as ammonia, 1,1-disubstituted hydrazines, primary amines, and sulphide and hydroxide ions. In the second case we have two-centre nucleophilic agents—hydrazine, hydroxylamine, and their derivatives. Ring rearrangements under the influence of one-centre nucleophilic agents usually reduce the replacement of the ring heteroatom via an intermediate ring opening step. The recyclisation reactions under the influence of two-centre nucleophilic agents, which involve nucleophilic additions and eliminations and obey the relations for the nucleophilic reactions of polar double bonds, are more complicated. For example, the two-centre nucleophilic agents involved in reactions with heterocycles containing polar double bonds (C=X, X=O, S, N, or P) have a higher reactivity than one-centre agents, due to the so-called α-effect[2,3]. Therefore they are also referred to as supernucleophilic agents[3]. This factor may affect significantly the rate-determining stages in the recyclisation reactions and can influence the mode of rearrangement. Moreover, two-centre nucleophilic agents can be involved in the ring rearrangement via one or both heteroatoms. Among supernucleophilic agents, the effect of hydrazine and its derivatives on heterocyclic systems has been particularly widely investigated, primarily in connection with the search for medicinal substances among heterocyclic derivatives of hydrazine.

Recyclisation reactions with hydrazines take place in both polar and non-polar solvents or in an excess of hydrazine in the temperature range 0 – 250°C.

One should bear in mind that the interaction of heterocycles with hydrazines can stop at the stage involving the substitution of labile groups in the heterocycle and the formation of ring-opening products or can be completed by a recyclisation the mode of which may be varied depending on structural factors and the reaction conditions. The expected reaction products may be isomeric. Hence one can understand the difficulties which frequently arise in the interpretation of the addition of hydrazines to heterocycles when a rearrangement of the latter is possible. This is reflected by frequent revisions of the mechanisms of such reactions initially suggested in the literature.

Despite this considerable number of published studies concerning the rearrangement of heterocycles, attempts to give a systematic account of the available data have not so

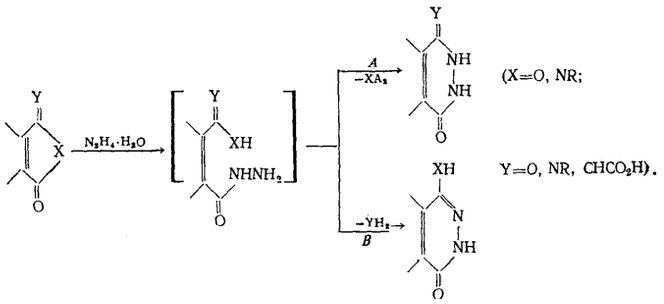
far been made. Although studies on the quantitative interpretation of recyclisation reactions have not been carried out, the available literature data based on synthetic investigations nevertheless permit definite generalisations and allow a systematic arrangement of the results. The present review includes the literature published in 1970 and partly in 1971.

II. RECYCLISATION REACTIONS OF HETEROCYCLES WITH TWO CENTRES IN THE RING SUSCEPTIBLE TO NUCLEOPHILIC ATTACK

1. FIVE-MEMBERED HETEROCYCLES

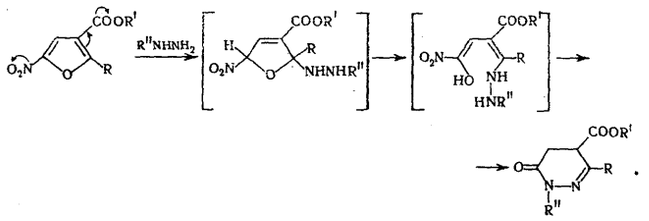
Five-Heterocycles with a Single Heteroatom

Recyclisation reactions with hydrazines are not typical for unsubstituted five-membered heterocycles with a single heteroatom in the ring. The presence of electron-accepting substituents in the ring renders both saturated and unsaturated and aromatic heterocyclic systems susceptible to nucleophilic attack. The rate of recyclisation is influenced by the electronic nature of the ring heteroatom (S > O ≫ NH), the presence of double bonds (cf. Feuer et al.[4]), and the position of activating substituents relative to the centres susceptible to attack. The outcome of the recyclisation reaction depends significantly on the positions of the centres susceptible to nucleophilic attack in the heterocycle. If they are in the α-positions relative to the ring heteroatom, then rearrangement to the pyridazine system usually takes place under the influence of hydrazines. Unsaturated five-membered heterocycles, including condensed heterocycles, containing exocyclic polar multiple bonds in both α-positions, react in this way:



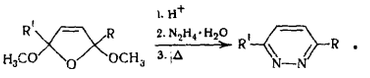
The mode of ring rearrangement—with elimination of the ring heteroatom (pathway *A*) or the α-substituent (pathway *B*)—depends on the nature of the substituent in the α-position. The occurrence of the reaction via both pathways has been noted only in the series of imino-oxoisoindolines [X = NH and Y = NR].[5] In other cases, where X = O or NR and Y = O or CHCOOH, the ring heteroatom is split off and a type *A* pyridazine structure is formed. The method of synthesis of type *A* cyclic hydrazides by the recyclisation of the corresponding cyclic anhydrides, which occurs when the reactants are simply mixed, is well known[6]. The anhydrides of 5,6-dihydro-*p*-dithi-in-2,3-dicarboxylic acids readily undergo a similar reaction, in particular with methyl- and *syn*-dimethyl-hydrazines[7,8]. Among reactions of this type, that of phthalidylideneacetic acid (X = O and Y = CHCOOH) with methylhydrazine to form oxophthalazineacetic acid has been used in the synthesis of physiologically active compounds[9].

Substituted furans, in which the αα′-centres susceptible to nucleophilic attack are activated by electron-accepting groups in the 2,4-positions of the ring, are recyclised under the influence of hydrazines into pyridazines[10], which resembles the ring rearrangement via pathway *B*:

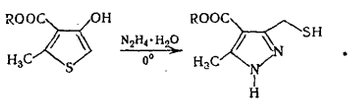


When R = H, the reaction takes place even at room temperature, but with R = alkyl it becomes strongly inhibited, which the authors believe is due to steric hindrance.

Recyclisation reactions with hydrazines in the furan series, where the αα′-centres of nucleophilic attack are activated saturated carbon atoms, have been described; they yield 3,6-substituted pyridazines which are otherwise difficult to obtain[11,12]:



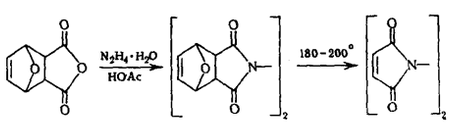
The thiophen ring with polar substituents in the ββ′-positions is readily transformed into the pyrazole system[13]:



Nitrogen-containing heterocycles undergo recyclisation with somewhat greater difficulty than their oxa- and thia-analogues. Nevertheless a modification of the Gabriel synthesis (the Ing—Manske reaction)[14,15], based on the addition of hydrazines to cyclic dicarboxylic acid imides (X = NR and Y = O), is known.

The rearrangements into pyridazine systems of a number of pyrrole derivatives (X = NH), in which the αα′-centres of nucleophilic attack are activated by substituents in the β-position of the ring, are also known[17,18]. 3-Benzoyl-4-isonitrosopyrrole undergoes recyclisation into the bicyclic isoxazolopyridazine system under these conditions[19].

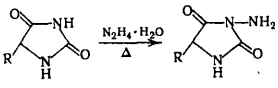
In the above reactions, the hydrazine molecule enters the ring via both nitrogen atoms, which results in the expansion of the initial ring. However, hydrazine can also enter the ring via only one nitrogen atom, which apparently depends to a considerable degree on the nature of the substituent in the hydrazine and on the medium. In acetic acid, cyclic dicarboxylic acid anhydrides give rise to the corresponding cyclic *N*-aminoimides on heating with hydrazine, phenylhydrazine, and acid hydrazides[20,21]:



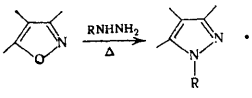
There are also literature data on the interconversion of cyclic hydrazides and imides[22–24]. Their formation depends sometimes on very slight changes in the structure of the anhydride[21,25]. Probably some of these reactions require further investigation.

Five-Membered Heterocycles with Two Heteroatoms

Five-membered heterocycles containing two nitrogen atoms in the ring (pyrazoles, imidazoles, and their hydrogenated analogues) do not undergo recyclisation reactions with hydrazines under the usual conditions. The presence of exocyclic heteroatoms appreciably activates such heterocycles. A simple preparative synthesis of aminohydantoins from hydantoins is known[26]:

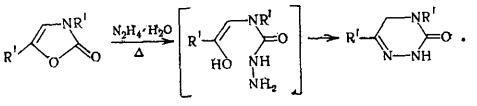


The capacity of five-membered heterocycles with two different heteroatoms to undergo recyclisation reactions depends on the relative positions of the heteroatoms in the ring. On heating with hydrazines, isoxazoles are converted into pyrazoles[27-30], but together with the latter other ring-transformation products were also detected:

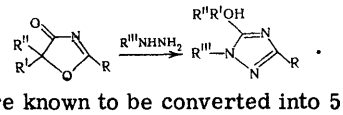


When the β-position of the isoxazole ring contains a powerful electron-accepting group (for example $R'' = NO_2$),[31-33] recyclisation with hydrazines, including even arylhydrazines, takes place particularly readily.

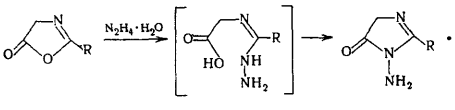
1,3-Oxazoles without activating substitutents are sensitive to hydrazinolysis but subsequent ring closure does not occur[34,35]. However, isomeric oxazolones and their derivatives containing an oxo group in addition to the multiple bond in the ring are capable of recyclisation when acted upon by hydrazines. Under these conditions, the outcome of the reaction depends significantly on the relative positions of the oxo-group and the ring multiple bond, which determine the mode of nucleophilic attack in the heterocyclic nucleus. On refluxing with hydrazine hydrate, 2-oxazolones yield triazinones[36]:



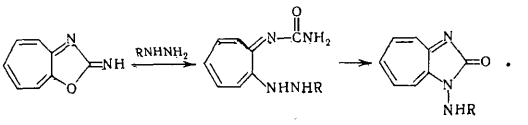
4-Oxazolones react vigorously with hydrazine forming triazoles[37]:



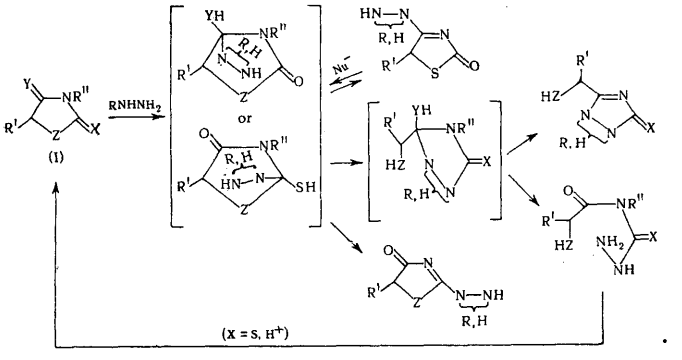
5-Oxazolones are known to be converted into 5-imidazolones when acted upon by hydrazine hydrate[38,39]. In contrast to both previous transformations, in this case hydrazine enters into the ring via only one heteroatom:



This difference in the behaviour of oxazolones probably depends on the activity of the nitrogen atoms of the hydrazine group in relation to the secondary electrophilic centre. If the latter is a carbonyl group, as in the first two cases, the interaction with the more basic β-nitrogen atom is preferable. On the other hand, the more strongly polarised α-atom interacts with the carboxy-group. The possibility of an interachange of the sites of attack in the heterocycle by the hydrazine molecule cannot be ruled out; this has been observed in the recyclisation of 2-imino-2*H*-cycloheptoxazole derivatives[40], in which *N*-amino-heterocycles are formed:



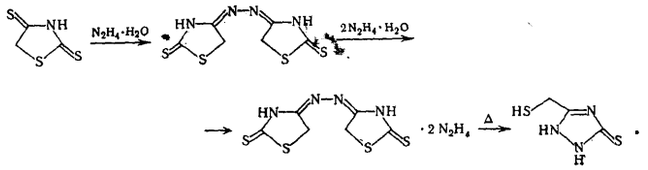
The oxa- and thia-zolidine rings activated by exocyclic heteroatoms in the 2- and 4-positions readily react with hydrazines with recyclisation into triazolones or triazolethiones[41]. Alkyl substituents in azolidinones (I, Z = S) inactivate them with respect to the addition of hydrazines, while *N*-arylated azolidinones are readily degraded[41,42]. The mode of reaction depends on the nature of the exocyclic heteroatoms in (I) [43,44] and also on the substituents in the hydrazine molecule, which determines the site of primary attack in the heterocycle by the hydrazine[45]. Depending on the reactivity of electrophilic centres in the azolidinone and the rate of removal of the XH_2 or YH_2 fragment, a hydrazonoazolidinone or triazolone (triazolethione) is formed. In isorhodanine (I, X = O, Y = Z = S), for example, the rate of elimination of hydrogen sulphide is much higher than the rate of reaction involving the 2-position in the ring and the rate of dissociation of the C — Z bond, which results in the formation of 4-hydrazinoazolidinone as the primary product. If conditions favouring such interaction are created (in the presence of nucleophilic agents), recyclisation into triazolone takes place. In rhodanines (I, X = Z = S, Y = O), the outcome of the reaction depends on the medium to an even greater extent[43,46]. 2-Hydrazinoazolidinones are formed only in an alcoholic medium, while in aqueous and alkaline media recyclisation into triazolethiones takes place:



When hydrazine acts upon rhodanines, it is possible to isolate an acyclic hydrazinolysis product, which is converted, depending on the conditions determining the competitive cyclisation reaction[47,48], into 2-hydrazinoazolidinone (in neutral solvents, on heating) or into a triazolethione (in alkaline media) or is reconverted into the initial rhodanine (in acid media). Recyclisation of substituted rhodanines into benzylidenehydrazonoazolidinones[49] and thiadiazine structures[46,50] has also been described.

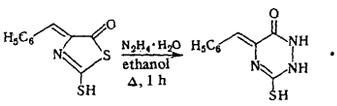
The recyclisation in the series of thiorhodanines has an unusual feature[43]. The presence of the reactive 4-thione group in the ring leads to the initial formation of an azine which reacts further with hydrazine in the presence of an

excess of the latter to form a saltlike adduct, which is converted on heating into a triazolethione:

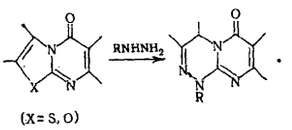


The recyclisation reaction of azolidine systems with hydrazine constitutes a convenient method for synthesising triazolones and triazolethiones with a mercapto-substituent in the side chain[51], which are difficult to obtain in other ways and which are of interest for pharmaceutical chemistry[52].

The conversion of benzylidenemercaptothiazolidine into mercaptobenzylidenetriazilone on refluxing with hydrazine, accompanied by ring expansion, has been described[53]:

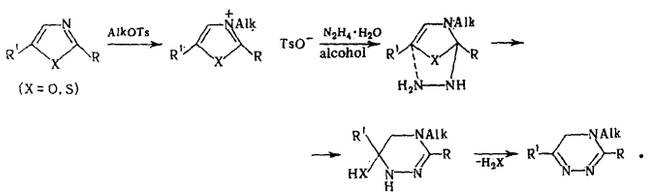


Condensed oxa- and thia-zole rings with a bridging nitrogen atom are converted in high yields into condensed cyclazine systems[54]. The reaction has a wide scope and in the pyrimidine series is of interest for the preparation of biologically active compounds:



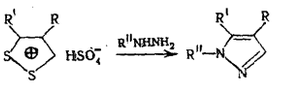
(X = S, O)

An effective method of increasing the reactivity of nitrogen-containing heterocycles in recyclisation reactions involves their conversion into a cationic state by the quaternisation of the ring nitrogen atom, as a result of which the electrophilic properties of the ring carbon atoms become much more pronounced. Even systems as stable as diaryloxazoles and diarylthiazoles are readily converted in this way into triazines[55,56]. Apart from this mechanism, which postulates a preliminary ring opening, yet another possibility of the rearrangement of cyclic cations via a quasi-1,2-addition of hydrazine to the ring has been considered[56]. In this case, after the initial attack by hydrazine on the azolium cation, the β-nitrogen atom interacts very rapidly with another electrophilic centre, which entails the dissociation of the C—X bridge bond:



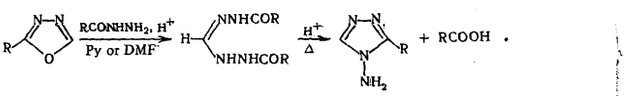
(X = O, S)

Dithiolium salts are very readily recyclised with replacement of the disulphide fragment in the ring by the hydrazine fragment[57,58]:

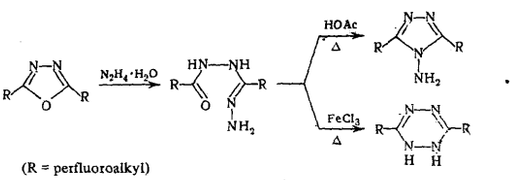


Five-Membered Heterocycles with Three Heteroatoms

Triazoles, particularly symmetrical triazoles such as pyrazoles, are extremely resistant to the action of hydrazine. Among five-membered heterocyclic compounds with three heteroatoms in the ring, derivatives of 1,3,4-oxadiazole have been most thoroughly investigated in recyclisation reactions under the influence of hydrazine. Despite their formal aromaticity, they are capable of exhibiting iminoether properties[59,60]. Alkyl- and monoaryl-substituted oxadiazoles are very sensitive to nucleophilic attack[61]. According to Eggert et al.,[62] they can be converted into aminotriazoles when acted upon by hydrazines:



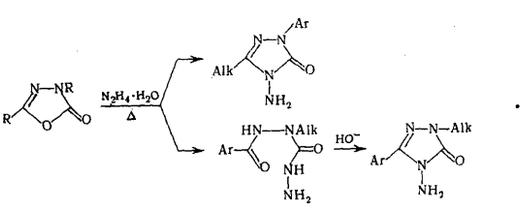
The recyclisation of perfluoroalkyl derivatives of oxadiazole under the influence of hydrazine hydrate has been described[63]. It takes place in two stages: ring hydrazinolysis (under mild conditions) and recyclisation into tetrazine or aminotriazole derivatives:



(R = perfluoroalkyl)

The substitution of both hydrogen atoms by aryl residues in the oxadiazole ring lowers its reactivity in recyclisation reactions with nucleophilic agents[61], probably in consequence of an increase of the overall aromaticity of the system[60]. Such oxadiazole derivatives do not react with hydrazines under the usual conditions. However, in the cationic state they are capable of recyclisation into *N*-aminotriazoles or tetrazines depending on the conditions[56]. In contrast to other azolium salts, the reaction is very sensitive to the nature of the anion.

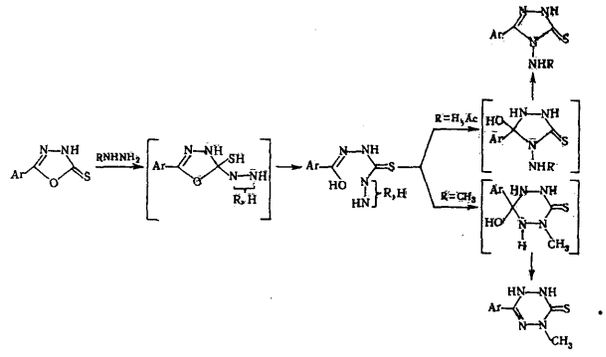
The presence in oxadiazoles of exocyclic oxo-, thio-, or amino-groups promotes the recyclisation reaction with hydrazine. On heating with stoichiometric amounts of hydrazine hydrate, oxadiazolones are converted into aminotriazolones[64]:



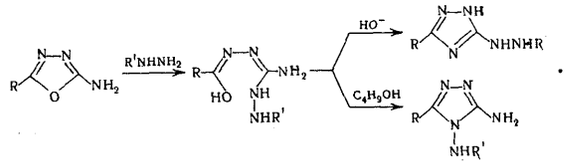
The reaction is very sensitive to the nature of the substituents and to the reactant ratio. On heating in an excess of hydrazine, oxadiazalones merely decompose into hydrazides[64-66].

On heating with hydrazines, oxadiazolethiones are capable of rearrangement via two pathways: into *N*-aminotriazolethiones (with unsubstituted hydrazines and acid

hydrazides) or into tetrazinethiones (with methylhydrazine)[67,68]. The reaction mechanism can be interpreted as follows:



The interaction of amino-oxadiazole derivatives with hydrazines has been widely investigated. It has been shown that, on heating with hydrazine, amino-oxadiazoles are capable of recyclising into *N*-aminotriazoles or hydrazinotriazoles[69]:



It has been stated[70,71] that the hydrazinolysis of the oxadiazole ring can involve both the $C_{(2)}-O$ and the $C_{(5)}-O$ bonds, depending on the nature of the substituent in the ring and in the amino-group. The reaction can lead directly to the triazole system[72-74] or, as usually happens when substituted hydrazines are employed, stops at the stage of the acyclic ring hydrazinolysis product. The subsequent mode of ring closure depends on the medium and the substituent[75-78].

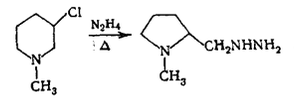
In the series of thiadiazoles, conversions into tetrazines under the influence of hydrazine are known[56]. Diarylthiadiazoles are inactive in relation to nucleophilic agents, but, like other azole systems, in a cationic state they are very vigorously recyclised into tetrazines under the influence of hydrazine.

2. SIX-MEMBERED HETEROCYCLES

The recyclisation reactions of six-membered heterocyclic compounds with two-centre nucleophilic agents take place not only with expansion or retention of the size of the initial ring, as in five-membered heterocycles, but can also involve ring contraction, although in the latter case hydrazine is involved via both its nitrogen atoms in the ring rearrangement. The outcome of the recyclisation is not determined solely by the positions of the centres of nucleophilic attack and the reactivity of the nitrogen atoms in the hydrazines. Energy factors can assume significant importance, for example in recyclisation reactions in the series of aromatic six-membered heterocycles with a single heteroatom, when there is a choice between the formation of a non-aromatic strained diazepine structure and an aromatic azole or pyridine system.

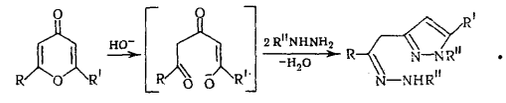
Six-Membered Heterocycles with a Single Heteroatom

Hydrogenated heterocycles—tetrahydro-γ-pyrone and tetrahydro-γ-thiapyrone and its sulphone as well as the thione analogues of both types of compound—do not react with amines but readily react with hydrazine, apparently owing to the α-effect[2], via the exocyclic heteroatom to form the corresponding hydrazones or azines[79], but there is no recyclisation. β-Chloro-*N*-methylpiperidine is known to undergo ring contraction when the halogen is replaced by hydrazine[80]:



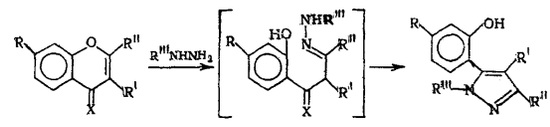
Unsaturated systems—pyrones, thiapyrones, and pyridones as well as their condensed analogues (chromones and coumarins)—readily enter into recyclisation reactions with two-centre nucleophilic agents. Although these compounds are represented in a non-ionic form, according to Schweizer[8] they can also assume the betaine-like structure of pyrylium, thiapyrylium, and pyridinium cations respectively, which show a very high tendency towards ring rearrangement, particularly on reaction with hydrazine. Although, depending on the nature of the heteroatom in the six-membered ring, the recyclisation reactions exhibit certain characteristic features, their outcome in the above series of compounds depends mainly on the position of the exocyclic heteroatoms, which determine the sites of nucleophilic attack in the ring. Therefore, fairly significant differences are observed between the recyclisation reactions of γ- and α-pyrones and their thio-analogues.

γ-Pyrone and its derivatives are readily converted under the influence of hydrazine or its substituted derivatives (on heating with the latter) into pyrazole derivatives[82-84]:



It is appropriate to mention here that the rearrangement of γ-pyrones under the influence of another two-centre nucleophilic agent (hydroxylamine) does not lead to isoxazoles, as might have been expected by analogy with the reaction quoted above, but to pyridone *N*-oxides[85]. Probably in this case the energy factors prevail over kinetic factors, since the isoxazole ring is less aromatic than the pyridine ring, while the pyrazole ring shows a high degree of aromaticity[81].

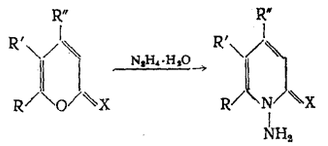
The condensed system—chromones and thiochromones—behave in recyclisation reactions with hydrazine analogously to γ-pyrones, being readily converted in the presence of catalytic amounts of alkali into *o*-hydroxyphenyl derivatives of pyrazoles in high yields[86-89]:



The authors believe[86,87] that the hydrazine molecule attacks primarily the C — O bond of chromone, since under analogous conditions the reactivity of both the carbonyl

and the thione group in these compounds in relation to nucleophilic agents is very low. When chromones and thiochromones react with arylhydrazines in a neutral or acid medium, only the corresponding hydrazones are formed; the latter are no longer capable of rearrangement under the influence of alkali[87].

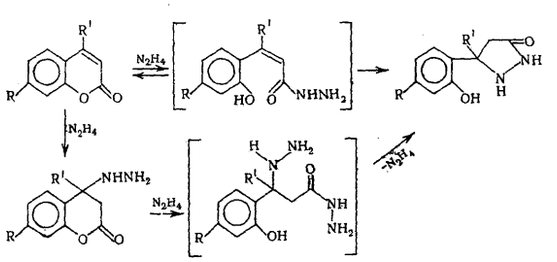
In contrast to γ-pyrones, α-pyrones and α-thiopyrones react with nucleophilic agents with much more difficulty. With hydrazine, they are converted fairly slowly into aminopyridones or aminopyridinethiones[90-92]:



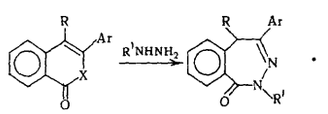
The rate of recyclisation of pyrones is appreciably influenced by the ring substituents. Aryl substituents in the hydrazine molecule hinder recyclisation. When α-thiopyrones react with phenylhydrazine, there is only a replacement of the sulphur atom by the hydrazine group[91,93]. It is noteworthy that the analogous reactions involving amines takes place with difficulty.

As stated above, condensed systems of the γ-pyrone type (chromones) are recyclised similarly to non-condensed analogues on reaction with hydrazine. In the series of α-pyrones, two condensed isomers are known—coumarins and isocoumarins—which differ very appreciably in the recyclisation reactions both from one another and from their monocyclic analogues. This is due to a different distribution of centres of nucleophilic attack which is greatly altered on condensation.

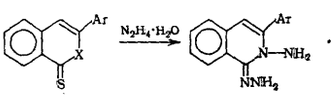
On heating with hydrazine hydrate, coumarins give low yields of pyrazoline derivatives[94]. The authors consider two alternative pathways for this reaction:



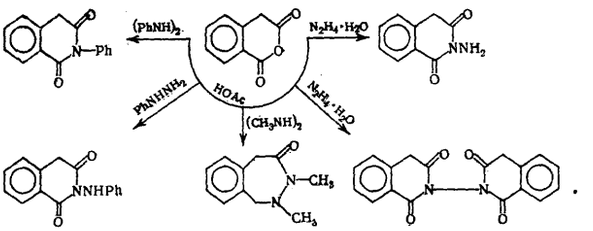
Under the influence of hydrazines, isocoumarins and isothiacoumarins recyclise into diazepinones[95-98], which are obtained in high yields:



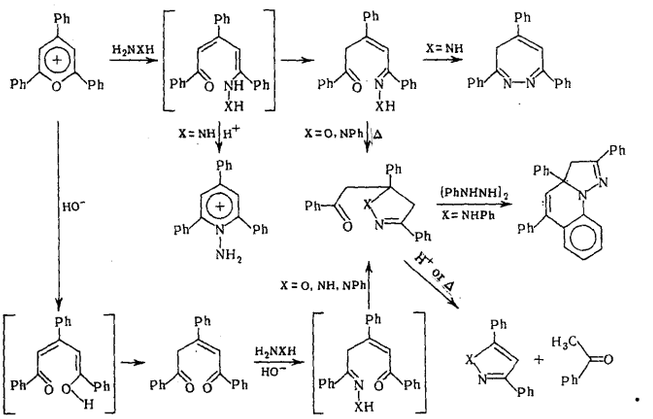
On the other hand, in the presence of an excess of hydrazine, thioisocoumarins and thioisothiacoumarins yield *N*-amino-1-hydrazonoisoquinolinones. In the case where equimolar amounts of the reactants are employed, there is merely a replacement of the thione sulphur atoms by the hydrazine group[99,100]:



In certain studies[101,102] the diazepine structure was attributed to the products of the recyclisation of homophthalic anhydride and its derivatives in the reaction with hydrazine. Subsequently these views were revised[103] and it was shown that, depending on the substituents in the hydrazine molecule, the reaction yields products with an imide structure and not azepines, which could not be detected either when the reaction was carried out in neutral solvents or in acetic acid. However, the formation of diazepine was noted when homophthalic anhydride reacted with *sym*-dimethylhydrazine:



The recyclisation reactions of pyrylium and pyridinium salts with hydrazines take place with exceptional ease. Their outcome is influenced significantly by the nature of the ring heteroatom and the substituents in both components, the nature of the anion, and also the medium. Depending on these factors, the cyclic cation can be transformed via three pathways: with ring expansion to the diazepine system, with ring contraction to the pyrazoline system and subsequent aromatisation by conversion into the pyrazole ring, and with replacement of the terminal heteroatom by the nitrogen atom and formation of *N*-aminopyridinium salts. The different types of recyclisation reactions in the series of pyrylium salts with two-centre nucleophilic agents (hydrazines and hydroxylamine) are most completely accounted for by Balaban's scheme[104-106] illustrated here for triphenylpyrylium perchlorate as an example:



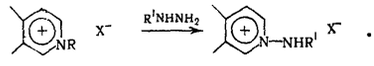
Triarylpyrylium salts are very readily converted into diazepines when acted upon by an excess of hydrazine hydrate[107]. However, pyrylium cations containing even only one methyl group in the α-position, for example 2-methyl-4,6-diphenyl- and 2,4,6-trimethyl-pyrylium perchlorates, are rapidly converted into pyrazoles in an excess of hydrazine hydrate in alcohol even at room temperature[108]. It has been shown[105,109,110] that the conversion into pyrazoles is more characteristic of pyrylium pseudobases. It is the main recyclisation pathway for pyrylium salts reacting with methylhydrazine[109] and benzenesulphonylhydrazine[110] and also for condensed pyrylium systems containing an activated γ-position and reacting with hydrazine hydrate (even in acetic acid)[111], but such

rearrangement takes place more slowly, usually on heating.

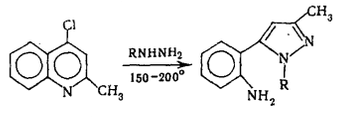
The interaction of hydrazine and its derivatives (phenylhydrazine and acid hydrazides) with pyrylium salts on heating in acetic acid leads to their recyclisation into *N*-aminopyridinium salts[105,112-116]. It has been shown[108,114] that 2,4,6-trimethylpyrylium perchlorate reacts with equimolar amounts of hydrazine hydrate even in an alcoholic medium with conversion into *N*-aminocollidinium perchlorate at a temperature as low as 0 – 5°C. Various substituted derivatives[117-119], including condensed pyrylium salts[108], were investigated in this reaction. The formation of two aromatic systems, pyrazole or pyridine, is probably due to competing processes which depend not only on the reactant ratio and the medium but also on the nature of the anion in the pyrylium salt[109], which affects the distribution of the electron density in the cyclic cation[120].

Balaban's scheme illustrated above includes also an interesting variant of the "pyrazole" recyclisation of arylpyrylium salts on heating in alcohol with an excess of phenylhydrazine, which involves a catalytic effect of the latter on the formation of the condensed pyrazoloquinoline system[121]. Under these conditions, neither hydrazine itself, nor hydroxylamine, nor various amines catalyse this reaction.

Recyclisation with hydrazines into *N*-aminopyridinium salts is characteristic of pyridinium salts[122-125]. It is also typical for their condensed analogues (isoquinolinium salts) and takes place under mild conditions in an alcohol – dioxan medium both with hydrazine and with its derivatives—phenylhydrazine, acid hydrazides, and thiosemicarbazide[125]:

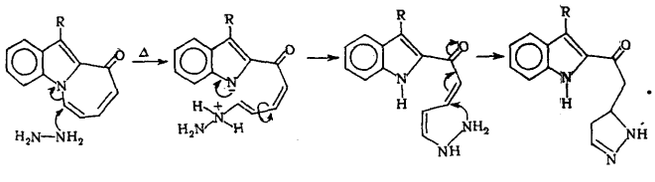


If the pyridinium ring contains an electronegative substituent in the 4-position, as in 4-chloroquinaldine, it is capable of recyclising into the pyrazole ring under the influence of hydrazine or phenylhydrazine[89]:



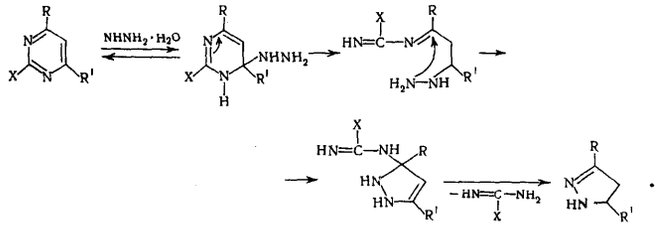
(R = H, Ph)

With increase of ring size, geometrical factors can assume a significant importance in recyclisation. For example, when indolinoazepinones react with hydrazine, the azepine ring is not converted into a six-membered derivative but into a five-membered derivative (pyrazoline)[126]:



Six-Membered Heterocycles with Two Heteroatoms in the Ring

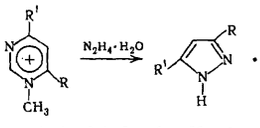
With increase of the number of heteroatoms in the ring, its electrophilic reactivity becomes enhanced and recyclisation reactions with hydrazine take place even without additional activating factors in the molecule. While unsubstituted or alkyl(aryl)-substituted pyridine bases do not undergo recyclisation under the usual conditions when acted upon by nucleophilic agents, pyrimidines are converted into the corresponding azole systems depending on the positions of the centres of nucleophilic attack. With sodium hydrazide[127], pyrimidines give high yields of pyrazole even at room temperature. With hydrazine hydrate and methylhydrazine, the conversion of pyrimidines into pyrazoles takes place under more severe conditions (130 – 200°C, 5 h).[128] It has been suggested that this process involves attack by the hydrazine molecule on the 4- or 6-position in the pyrimidine ring with its subsequent recyclisation, which is completed by aromatisation as a result of the elimination of a urea moiety[129]:



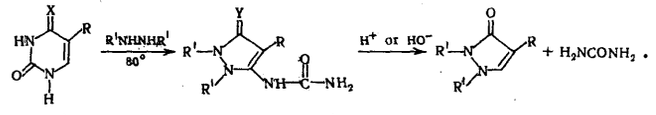
(X = H, HO, NHR, SR, Ar)

The recyclisation reactions of pyrimidines are extremely sensitive to the nature and position of the ring substituents. Electron-donating substituents (alkyl, aryl, OH, NH_2, SCH_3) in the 2- and 4-positions of the pyrimidine ring do not alter the above mode of reaction but polar groups appreciably accelerate it[130-134]. The electron-donating properties and the steric effect of the methyl group in the 4- or 6-position inhibit the reaction, which requires higher temperatures[129]. Depending on the substituents in the heterocyclic nucleus[131], in certain cases the interaction can lead only to hydrazinolysis products.

The quartenisation of one of the nitrogen atoms in the pyrimidine ring greatly facilitates the above recyclisation reaction without altering its outcome[129]:



In the series of certain biologically important pyrimidine derivatives, the following sequence of their reactivities in relation to hydrazine has been noted[133,134]: uracil, cytosine, thymine. In the reaction with methylhydrazines it is possible to isolate intermediates containing the ureide group, which is subsequently split off under the influence of alkali or acid[133]:

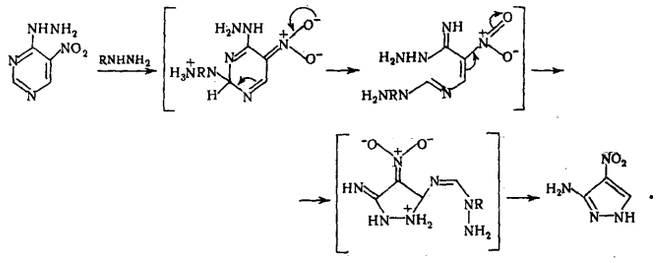


(R' = H, CH_3; X = O, NH; Y = O, NH, NNHR')

The hydrazinolysis of purines, pyrimidines, and the related nucleosides and nucleotides, which is completed by the formation of pyrazole systems, has been widely investigated in order to identify the pyrimidine bases[135-140].

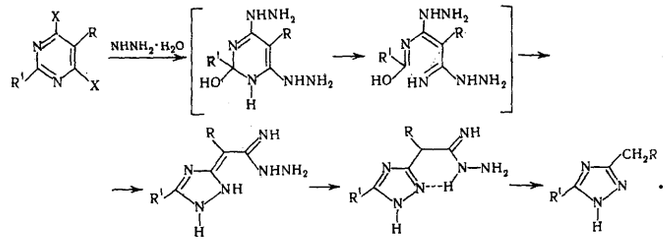
The introduction of powerful electron-accepting substituents into the pyrimidine ring has a significant influence on the distribution of electron density in the latter[130], with a corresponding alteration of the centres of nucleophilic attack, which influences the mode of the

recyclisation reaction. The effect of the nitro-group is particularly pronounced; when it is present in the 5-position, the recyclisation mechanism is significantly modified[141,142]. The reaction occurs even at room temperature in the presence of an excess of hydrazine (or methylhydrazine) and leads to aminopyrazoles. In contrast to the mechanism quoted above[129], nucleophilic attack by the hydrazine molecule on the 2- or 6-position in the heterocycle, its opening at the 2 — 3 bond, and recyclisation are suggested[142]. Under these conditions, the $N_{(3)}$ atom is converted into an exocyclic amino-group and the residue comprising the $N_{(1)} - C_{(2)}$ fragment of the pyrimidine ring is split off:



The above mechanism is confirmed by the reaction of methylhydrazine with 6-hydrazino-5-nitropyrimidine[142] which resulted in the isolation of the same pyrazole and not its methyl analogue.

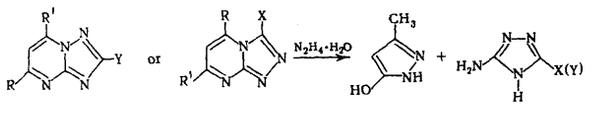
Pyrimidines containing polar substituents (OCH_3, $NHNH_2$) in the 4- and 6-positions are capable of transformation via a different pathway (with rearrangement of the ring to triazole)[128,143]. The reaction takes place with a 30 — 90% yield but under fairly severe conditions (210°C, 5 h):



According to van der Plas and Jongejan[143], the elimination of the carbazide residue is promoted by the formation of a hydrogen bond.

Special cases of the recyclisation of pyrimidines, occurring under severe conditions probably by ring fragmentation, are also known. Thus, on refluxing with hydrazine for 24 h, 4-hydroxy-6-methyl-2-phenylpyrimidine gives a 75% yield of 4-amino-3,5-diphenyl-1,2,4-triazole together with 3-methyl-5-pyrazolone.

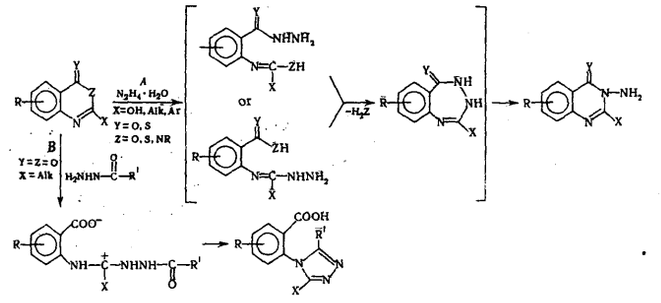
The recyclisation of condensed derivatives of pyrimidine containing the triazole ring, which is very resistant to the action of hydrazine, involves only the pyrimidine ring. It results in the formation of the corresponding pyrazoles and triazoles[144]:



(R = CH_3; R' = OH; X = SH, SAlk; Y = SAlk, NH_2, H)

The mode of reaction is not altered as the substituents (X, Y) in triazaindolizine are varied, but it is sensitive to substituents in the hydrazine molecule and the reaction does not occur when phenylhydrazine is employed.

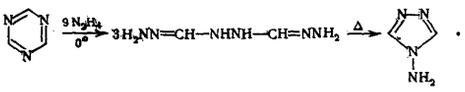
The recyclisation of the heterocyclic nucleus when hydrazine adds to quinazolones[145,146], benzoxazolones[147], and their thioanalogues[148], where a six-membered heterocyclic nucleus containing two different heteroatoms is condensed with the benzene ring, yields either *N*-aminoquinazolones (pathway *A*) or pyrazole derivatives (pathway *B*):



The rearrangement of benzoxazinones on reaction with benzoyl hydrazide, semicarbazide, and carbohydrazide leads to the formation of quinazolones. In the reaction with dicarboxylic acid dihydrazides, quinazolones are formed together with triazoles. In the reaction with formyl-, acetyl-, cyano-, nitro-, phenoxy-, and diaminoacetyl-hydrazines, triazoles are the main reaction products[147,149]. Owing to the higher nucleophilicity of the unsubstituted β-nitrogen atom compared with the α-nitrogen atom in the hydrazine fragment, the transformation of such systems via pathway *A* should occur, as suggested for benzothiazinethiones[148], via a diazepine structure with its subsequent rearrangement (of the type described below) to quinazoline, which is favoured by energy factors. If there is an acyl substituent at the β-nitrogen atom, the α-nitrogen atom, which has a steric advantage in this case, is probably involved directly in ring closure. However, such recyclisation is much slower. On the other hand, in the formation of triazoles by pathway *B*, the reactivity of the second competing carbonyl centre in the substituted hydrazine is decisive.

Six-Membered Heterocycles with Three and More Heteroatoms

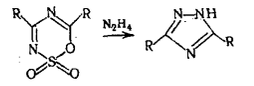
In the series of triazines, the mode of reaction with hydrazines is determined to a considerable degree by the nature of the substituents in both the ring and in the hydrazine derivatives employed. Unsubstituted *sym*-triazine in anhydrous hydrazine undergoes complex hydrazinolysis at a temperature as low as 0°C with subsequent recyclisation into *N*-aminotriazole:



Sym-disubstituted hydrazines do not react under these conditions, but semi- and thiosemi-carbazides and aminoguanidine yield respectively 3-hydroxy-, 3-mercapto-, and 3-amino-1,2,4-triazoles[150-153].

Among the recyclisation reactions of heterocycles containing several different heteroatoms in the ring, the

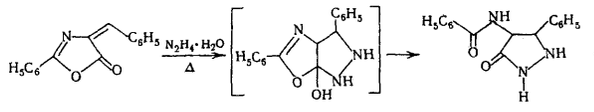
conversion of 4,6-diaryl-1,2,3,5-oxathiadiazine-2,2-dioxides into 3,5-diaryl-1,2,4-triazoles is known[154,155]:



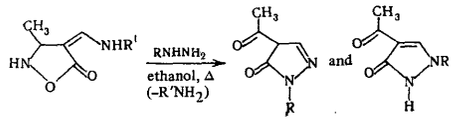
III. RECYCLISATION REACTIONS OF HETEROCYCLES WITH ONE CENTRE IN THE RING SUSCEPTIBLE TO NUCLEOPHILIC ATTACK

The recyclisation reactions of heterocyclic compounds containing one centre of nucleophilic attack in the ring and another in the side chain are nucleophilic addition or addition — elimination reactions involving polar multiple bonds. They can take place via two main mechanisms: with the intermediate formation of a bicyclic system and subsequent rupture of the initial ring or with preliminary ring opening after the initial addition of hydrazine and subsequent ring closure. The recyclisation pathway should be influenced mainly by steric factors and by the reactivity of the reaction centres. If the reaction centre in the ring adjoins the side chain but its reactivity is lower (or almost the same) than that of the electrophilic centre in the side chain, one may expect the reaction to proceed via an intermediate bicyclic compound. If, however, owing to the higher reactivity of the centre of nucleophilic attack, the primary addition of hydrazine begins at the heterocyclic nucleus, ring opening can take place initially†.

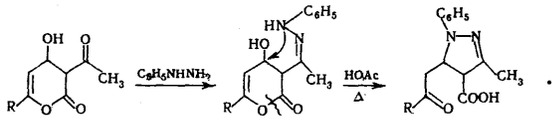
In the series of five-membered heterocyclic compounds, azlactones are probably recyclised[156] via the first pathway into the corresponding pyrazolidinones on heating with hydrazine:



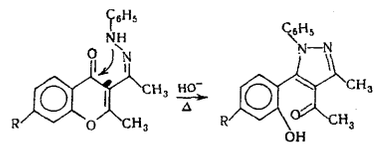
A similar reaction has been described also for isomeric isoxazolidinones[157]:



In the series of six-membered heterocycles such reactions are known for pyrone derivatives[158] on heating with substituted hydrazines in acetic acid:

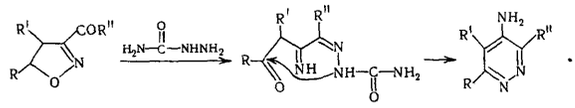


With condensed pyrone analogues (chromones), a similar conversion into pyrazole derivatives takes place under the influence of alkali[86]:



† See also Wamhoff and Korte[255].

The recyclisation of diacylfuroxans into dihydroxyiminopyrazolines[159] and of *N*-chloroethyl-2-oxazolidinone into N-aminoimidazolinone[160] under the influence of hydrazines has been described in the literature; the authors believe that it proceeds via the intermediate opening of the initial ring, which is a general characteristic of such systems[161]. The conversion of heterocycles in which the reaction centre in the ring does not adjoin the side chain with another electrophilic atom may proceed similarly and therefore the formation of a bicyclic system is hindered by steric factors. Under the influence of semicarbazide, acyl derivatives of isoxozole are converted into pyrazines[19,162]:



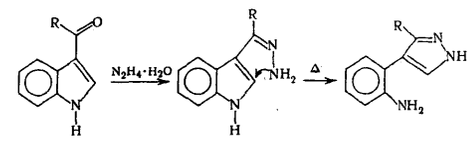
IV. RECYCLISATION REACTIONS DUE TO HETEROCYCLIC REARRANGEMENTS INVOLVING THE HYDRAZINE MOIETY IN THE MOLECULE

1. THE ALBERTI — BOULTON — KATRITZKY REARRANGEMENT OF HETERYLHYDRAZINES

The Alberti — Boulton — Katritzky rearrangement is a special case of recyclisation reactions involving one centre of nucleophilic attach in the ring. Heterocycles containing an electrophilic centre adjoining the ring heteroatom with a substituent containing the hydrazine group in the α-position relative to the electrophilic centre are capable of undergoing such rearrangement. The rearrangement consists in the formation of a new ring via an intramolecular interaction of the hydrazine nitrogen atom in the side chain with the electrophilic centre of the initial heterocycle.

Both a carbon atom and heteroatoms such as nitrogen (usually in the sp^2-hybridised state) can behave as an electrophilic centre in the heterocycle. The rearrangement takes place under the action of heat or bases.

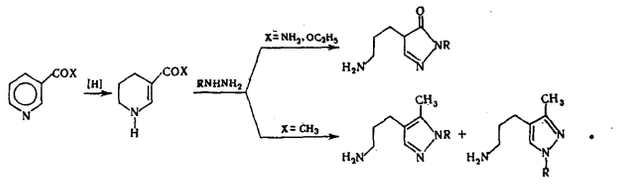
The rearrangement of heterocycles with a carbon atom as the electrophilic centre was discovered by the Italian chemist Alberti[163], who showed that, when 3-acetylindoles are heated in an alcoholic medium with hydrazine hydrate, a hydrazone is formed initially and then isomerises further to a pyrazole derivative[163,164]:



Alberti suggested that heterocyclic compounds containing the group $-X-C=C-CO-R$, where X is the heteroatom, undergo a similar recyclisation when acted upon by hydrazine[165]. The reaction was extended to other classes of heterocycles containing an acyl substituent in the β-position relative to the ring heteroatom—the thionaphthene, pyrrole, quinoline, and γ-pyrone series, from which pyrazole derivatives were obtained. However, whereas in the indole, γ-pyrone, and γ-chromone series the rearrangement takes place when the initial components are refluxed in alcohol, in the pyrrole and quinoline series heating to 160 — 165°C in an autoclave is required[166-168].

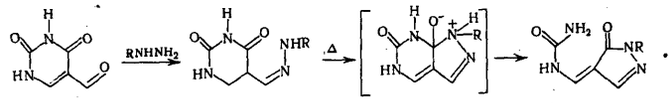
The conditions governing the rearrangement were examined in a series of studies by Alberti[169-174].

Recyclisation reactions of various heterocycles with an electrophilic centre in the α-position relative to the acyl group were described later. These reactions evidently proceed via the same rearrangement. They usually occur when the heterocycle is heated briefly with hydrazine but the intermediate hydrazone was not always identified. Thus pyrazole derivatives were obtained in high yields from acyltetrahydropyridines[175,176]:

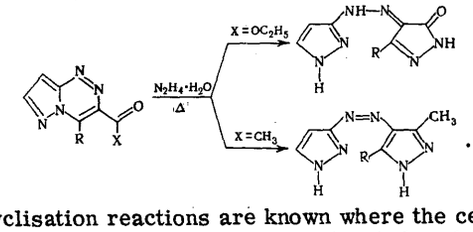


The reaction can serve as a convenient method of synthesising aminoalkylpyrazolones or pyrazoles from acylpyridines, which are readily reduced to tetrahydroderivatives.

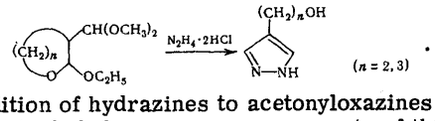
In the above examples, an olefinic carbon atom served as a centre of nucleophilic attack in the ring. In pyrimidine derivatives [177] the carbon atom of a carbonyl group functions as a centre of this type:



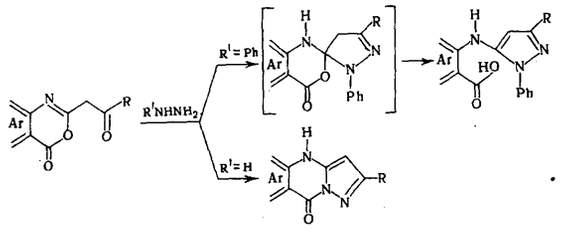
The rearrangement can occur also in systems such as pyrazolotriazines[178], where the electrophilic centre adjoins a bridging heteroatom:



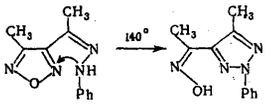
Recyclisation reactions are known where the centre of nucleophilic attack in the ring is a saturated carbon atom subjected to the influence of two electronegative heteroatoms—endocyclic and exocyclic. Here the rearrangement is based on a substitution reaction. Such rearrangements occur readily in both five-membered and six-membered heterocycles[82]:



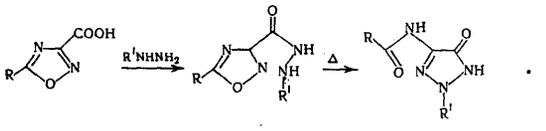
The addition of hydrazines to acetonyloxazines can probably be included among rearrangements of this kind [179,180]; the outcome of the reaction depends in this case on the presence of substituents in the hydrazine. Here isomerisation proceeds via an intermediate spirocompound:



Boulton and Katritsky[181-183], who studied heterocyclic isomerisations, greatly extended the scope of this rearrangement and established that a nitrogen atom can also serve as a centre of nucleophilic attack in the ring. For example, acetylfurazan phenylhydrazone can be converted into a 1,2,3-triazole system on heating in dimethyl sulphoxide in the presence of alkali[181]:



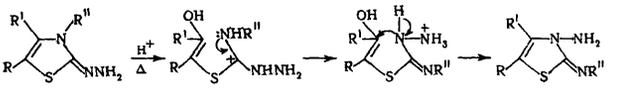
Hydrazine derivatives of 1,2,4-oxadiazoles[184] and isoxazoles[185,186] isomerise similarly into triazole. The rearrangement can proceed not only with participation of a base but also under the influence of heat. 1,2,4-Oxadiazole-3-carboxylic acid hydrazides isomerise almost quantitatively into a triazole system[187] not only under the influence of a base but also on heating above the melting point:



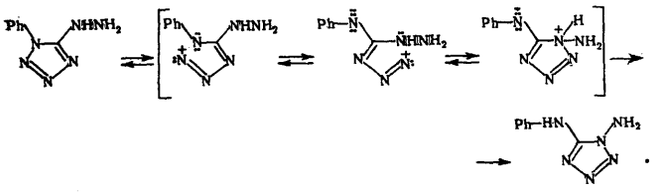
It is noteworthy that in almost all the cases considered a similar rearrangement occurs also in the presence of another two-centre nucleophilic agent—hydroxylamine.

2. THE DIMROTH REARRANGEMENT OF HYDRAZINE CONTAINING HETEROCYCLES

The Dimroth rearrangement consists in the interchange of endocyclic and exocyclic heteroatoms (together with their substituents) adjoining the same carbon atom in the ring and proceeds via ring opening in the presence of acids and bases or under the influence of heat. For example[188,189]:



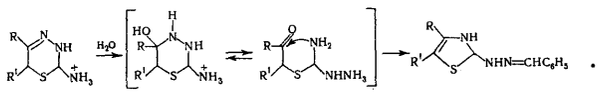
Dimroth observed the rearrangement in the series of 5-amino-1,2,3,4-tetrazoles[190,191]. Nirenburg and Postovskii described a similar thermal isomerisation and its mechanism for 5-hydrazino-1,2,3,4-tetrazoles[192]:



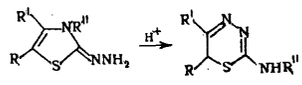
Hydroxylic solvents are the most suitable media for such isomerisations.

A number of general relations noted by Wahren[193] for the Dimroth rearrangement are also typical for heterocyclic hydrazines, although the latter have their own characteristic features. Here the rate of isomerisation should depend on the electron density at the α-carbon atom[194-197]. An important characteristic of the rearrangements of hydrazine-containing heterocycles is that the hydrazine group can participate in the isomerisation via the α- or β-nitrogen atom. Frequently the α-nitrogen atom is more reactive regardless of whether the β-atom is substituted or free. This may be due to the marked

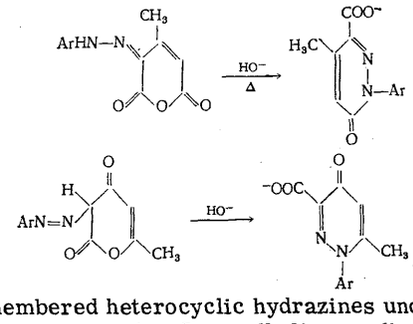
polarisation of the α-nitrogen atom of the hydrazine group in the acyclic intermediate owing to the influence of electronegative substituents. As a result, it can give up a proton to the polar medium, becoming more nucleophilic in the ring closure reaction. This variant corresponds to the Dimroth rearrangement where the ring sizes before and after isomerisation remain unchanged[193]. From the standpoint of the process mechanism, this limitation is hardly obligatory for hydrazine-containing compounds. When 3-amino-5,6-dimethyl-1,3,4-thiadiazine hydrochloride is heated with benzaldehyde in alcohol, ring contraction takes place with formation of the corresponding thiazolehydrazone[198]. Such recyclisation fits quite satisfactorily within the framework of the Dimroth rearrangement, which follows from the following mechanism:



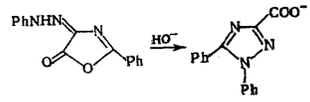
The example considered constitutes, as it were, a retrorearrangement in relation to the isomerisation of heterocyclic hydrazines accompanied by ring expansion where the hydrazine residue is involved via the β-nitrogen atom. Thus the conversion of thiazolehydrazones into thiadiazines is known[199]:



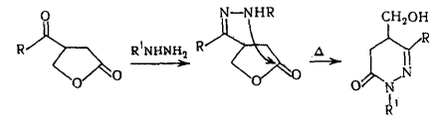
The isomerisation reactions of hydrazine-containing heterocycles accompanied by the exchange of complete fragments of the ring are probably related to the Dimroth rearrangement. For example, the isomerisation of hydrazinopyrones to pyridazones, which occurs on heating in an alkaline medium[200-202], constitutes an exchange of the exocyclic hydrazine group in the β-position in the ring with the endocyclic —CO—O fragment. Here the hydrazine group does not adjoin the ring heteroatom and it enters the ring via the β-nitrogen atom and not the α-atom:



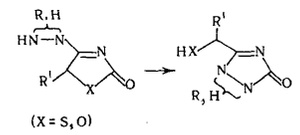
Five-membered heterocyclic hydrazines undergo a similar rearrangement. In an alkaline medium, 4-phenylhydrazono-2-phenyloxazolin-5-one undergoes a very rapid quantitative conversion even at room temperature into 3-carboxy-1,5-diphenyl-1*H*-1,2,4-triazole[203]:



Rearrangements involving the β-nitrogen atom of the hydrazine group are regarded in the literature also as transannular addition of hydrazine[126] which does not proceed via a preliminary hydrazinolysis of the initial ring. An attack on the ring electrophilic centre by the hydrazine β-nitrogen atom has been suggested; it takes place via a transannular mechanism and leads to an intermediate bicyclic system in a manner similar to the formation of bicyclic acetals and lactones in the pyran series. For this purpose, the hydrazine group or the substituents containing it should be located at a tetrahedral carbon atom in a ring in which there is a sterically accessible electrophilic centre. According to Wamhoff and Korte[204], the hydrazones of β-acyl-γ-lactones isomerise on heating to pyridazines via a transannular mechanism:



In heterocyclic compounds where the hydrazine group is attached to an unsaturated carbon atom, transannular rotation is difficult owing to the rigidity of the bond. However, it becomes possible under the influence of alkalis or other nucleophilic agents, which results in a tetrahedral configuration of the carbon atom linked to the hydrazine group. The isomerisation of hydrazinoazolidinones[41,205-207], occurring in alkaline media or on heating, has been interpreted in this way. Here a second molecule of the hydrazinoazolidinone behaves as the nucleophilic agent:



(X = S, O)

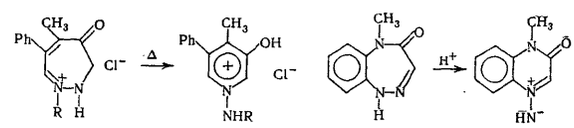
Various substituted hydrazinoazolidinones (derivatives acylated at the hydrazine group, hydrazones, and azines) undergo similar rearrangements.

The Dimroth rearrangement can occur in complex reactions and is accompanied by the cleavage of unstable components of the molecule. For example, the recyclisation of uloses into pyrazole derivatives in an acid medium, via the corresponding hydrazone, is known[208,209]. Alkaline cleavage of imidazophthalazine[5], the recyclisation of 2-hydrazino-4-hydrazono-3-phenylquinazoline into 2-anilino-4-hydrazinoquinazoline[210], etc.[113,211] also involve the Dimroth rearrangement.

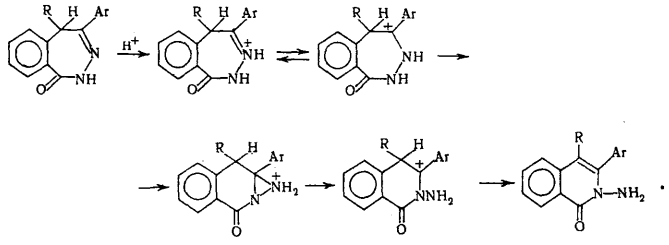
3. REARRANGEMENT OF CYCLAZINES

Heterocyclic compounds containing an endocyclic hydrazine group and multiple bonds are capable of a rearrangement involving the contraction of the ring by one nitrogen atom, which passes to an exocyclic *N*-imino- or *N*-amino-group. The rearrangement, which takes place under the influence of heat or an acid, is characteristic of various six-membered and seven-membered azine systems: diazines, triazines, tetrazines, and diazepines.

Depending on the structure of the initial cyclazine, the final isomerisation products may be betaines or cyclic *N*-amines. 4-Oxo-2,3-dihydro-1,2-diazepines[212] or 4-oxo-1*H*-4,5-dihydro-1,2,5-benzotriazepines rearrange to betaines:

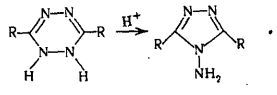


If there is a possibility that the charge in the betaine structure may be compensated by the β-elimination of a proton, the final product is a cyclic *N*-amine[98]:

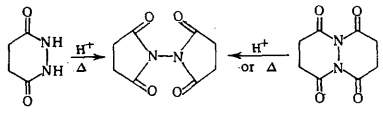


The isomerisation of cyclazines may be regarded as an endocyclic sextet rearrangement. The above scheme shows that its mechanism involves[98-100,141,212,213] an endocyclic interaction between the nitrogen atom of the hydrazine moiety and an activated unsaturated carbon atom or a carbonium centre with formation of an intermediate three-membered condensed ring, the opening of which results in the liberation of the amino group. The role of the acid as a catalyst reduces to the protonation of the heteroatom adjoining the sp^2-hybridised carbon atom. However, one should note that, under certain conditions, one cannot rule out the possibility that such a rearrangement can also proceed via a preliminary hydrolytic ring opening at the azomethine linkage with subsequent ring closure under acid conditions, as rule via the α-nitrogen atom of the hydrazine group.

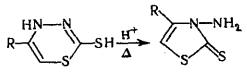
The cyclic *N*-amine rearrangement is very characteristic of tetrazines, which are readily converted in an acid medium into *N*-aminotriazoles[214,215]:



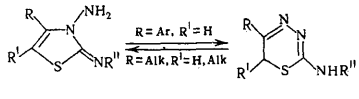
The isomerisation of cyclic hydrazides[216,217], including hydrazides condensed with ring systems[216,218] and their thioanalogues[219], allows a ready synthesis of *NN'*-bis-succinimides, *N*-aminothiazolethiones, and *N*-aminohydantoins:



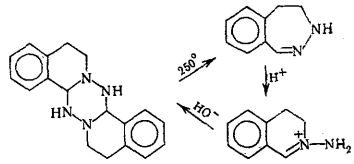
Cyclic thiohydrazides and thiadiazinethiols[219], for which a Dimroth rearrangement might have been expected in an acid medium, undergo preferentially the cyclic *N*-amine isomerisation:



Depending on the structure of the compound, it is possible to achieve the reverse transition from cyclic *N*-amines to cyclazines. Such interconversion has been described for the thiadiazine — *N*-aminothiazole series[199] and others[22,23]:

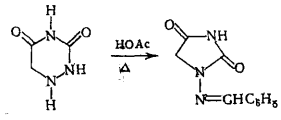


The cyclic *N*-amine rearrangement and its retrovariant were observed by Schmitz and Ohme[220].

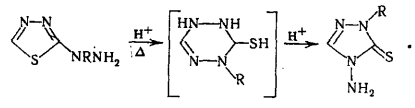


One may suppose that the retrorearrangement also proceeds via the intermediate formation of a three-membered condensed ring.

The cyclic *N*-amine rearrangement can occur in combination with other reactions. On heating with aldehydes, usually in the presence of acetic acid, cyclic hydrazides are converted directly into the corresponding cyclic *N*-arylideneamines[217]:



Complex recyclisation reactions may be also accompanied by the above type of isomerisation, as happens, for example, in the conversion of hydrazinothiadiazoles into *N*-aminotriazolethiones[221]:

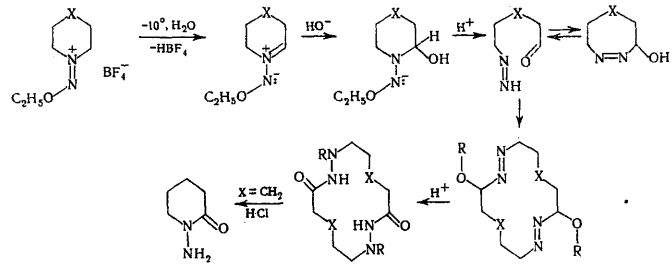


On reaction with hydrazines, certain isochromones recyclise directly into isoquinolinones[98].

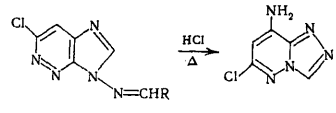
V. OTHER REARRANGEMENTS AND RECYCLISATIONS OF HYDRAZINE-CONTAINING HETEROCYCLES

The reactions of heterocycles involving hydrazines which are described in the literature can be usefully examined separately owing to their characteristic features. Here we shall be concerned also with the recyclisation reactions of small rings under the influence of hydrazines.

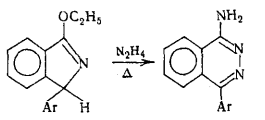
In an alkaline medium under very mild conditions, substituted iminopiperidinium and iminomorpholinium salts undergo a dimerisation recyclisation with formation of a macroring, which in the case of piperidinium recontracts under the influence of acids into the aminopiperidine system[222,223]:



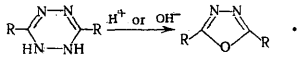
The recyclisation of imidazopyridazine derivatives into triazolopyridazines, which occurs on heating in an acid medium, was described recently[224]:



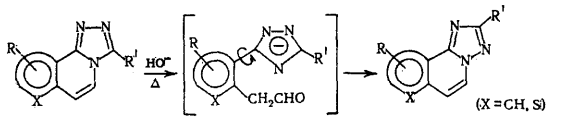
The reaction of 1*H*,1-aryl-3-ethoxyisoindolinenes with hydrazine, with recyclisation into benzopyridazines, is somewhat unusual:



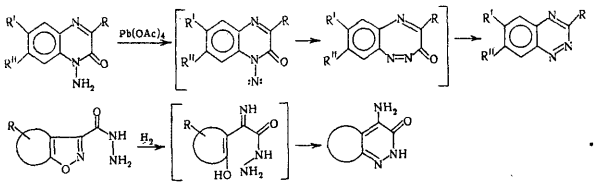
Certain substituted tetrazines are converted in acid or alcoholic alkaline media into oxadiazoles and not into *N*-aminotriazoles. The reaction is greatly influenced by the nature of the ring substituent[56,226-228]:



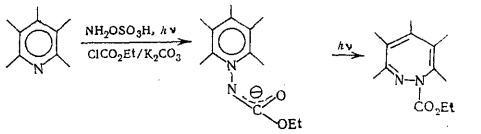
Thermal recyclisation of tetrazines into pyrazoles is also known[229]. On heating in alkaline media, triazoloisoquinolines and triazolothienopyridines undergo an isomerisation involving the hydrazine moiety of the triazole ring[230]:



In many cases recyclisation reactions involving the hydrazine group in the molecule can occur as a result of oxidation — reduction processes[231-233]:

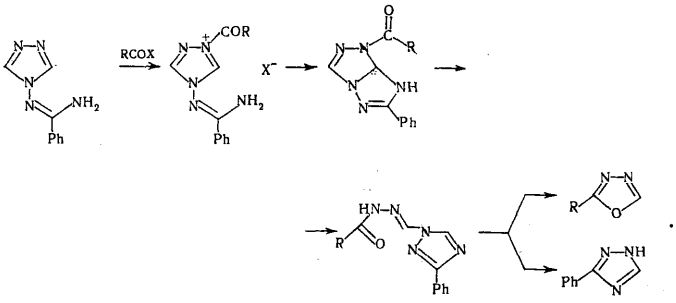


Photochemical recyclisation reactions of heterocycles involving the hydrazine moiety are known for a series of five-membered[234] and six-membered heterocycles, in particular the conversion of *N*-aminopyridines into diazepines[235,236]:

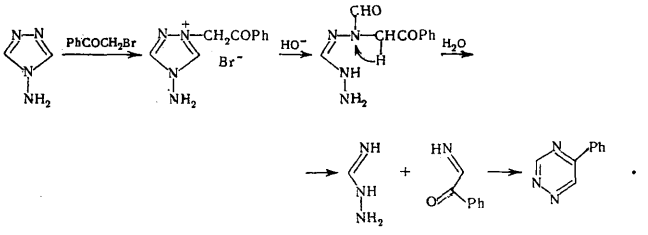


Relay Syntheses

In a series of studies by Becker and coworkers[237-244], recyclisation reactions of hydrazine-containing heterocycles, called relay syntheses, are described. They consist of ring opening and closure, for example the formation of triazole rings, accompanied by fragmentation. Despite their complex mechanism, these syntheses usually take place smoothly and they are of preparative value. As an example, one may quote the coupled recyclisation reaction of triazole derivatives[239]. It can be divided into stages or can be carried out successfully in one stage:



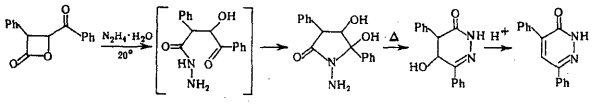
The authors believe[240] that relay syntheses can be achieved via complete fragmentation of the ring with its subsequent reassembly into a new ring, as shown in the following scheme:



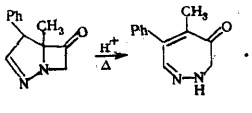
Certain recyclisation reactions in the series of other heterocycles (oxadiazolopyrimidines[245] and amino-oxadiazolium salts[246]), which permit a conversion into triazole and imidazole derivatives, can also be included among the relay syntheses.

Recyclisation Reactions of Small Rings

The recyclisation reactions of small rings under the influence of hydrazines are accompanied by ring expansion. Cyclic β-ketoesters form bicyclic pyrazole derivatives. According to Jacobs[247], the synthesis of 3-methyl-1-phenylpyrazol-5-one from diketen and phenylhydrazine is of industrial interest. In the series of β-lactones, the rearrangement of a four-membered ring to a six-membered ring takes place by successive recyclisation; under certain conditions, the intermediate heterocycles were isolated and identified[248]:



The bicyclic pyrazoline system condensed with a four-membered ring via a C — N bond isomerises to a diazepine structure on heating in a weakly acid medium[249,250]:



Three-membered rings usually rearrange to five-membered rings and more rarely to six-membered rings, mainly depending on the nature and positions of the substituents in the small ring. Reaction involving the recyclisation of aziridines into pyrazoles[247], pyrrolines[251], and imidazoles[252], of azirines into a six-membered triazine system[253], and of oxirans into pyrazoles[247,254], are known.

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