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Molecular rearrangements of five-membered ring heterocycles are conveniently classified in five categories based on the number of participating side-chain atoms. These include the rearrangements which operate by a ring contraction-ring expansion mechanism, the Dimroth rearrangement, the Cornforth rearrangement, the Boulton-Katritzky scheme, the bond-switch rearrangements with sulfur as the pivot atom, and many other isolated cases. A concise description of these rearrangements in the monocyclic series is given with particular emphasis on the thermal reactions. The photoisomerizations have been included only when necessary for discussion, since an excellent recent review exists on this topic (ref [9]).

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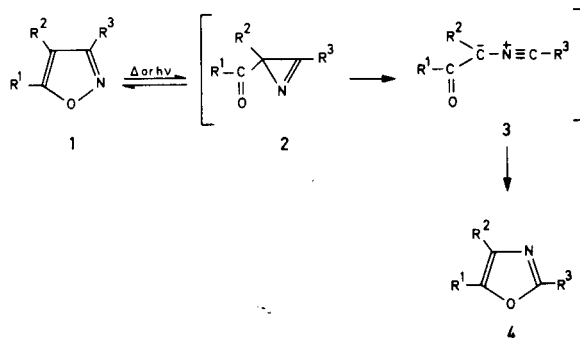
Molecular rearrangements constitute an important aspect of ring-transformation reactions of heterocyclic compounds [1]. Several types of rearrangement have already been reviewed, but a general classification has never been made. We present here a survey of molecular rearrangements of monocyclic 5-membered heterocycles and provide a classification which is based simply on the number of side-chain atoms involved during the rearrangement. The material for this review has been selected on the basis of interest and need for discussion, primarily from publications on aromatic heterocycles.

A few comments on the terminology are in order. In our opinion, the terms mononuclear or monocyclic rearrangement, used by some authors, also apply to polycyclic structures where only one ring is transformed. Most of the known heterocyclic rearrangements then come under this definition. Therefore, in order to avoid confusion, we prefer to describe the reactions discussed below as rearrangements of heteromonocycles. When the transformation furnishes the same ring system (e.g. oxazole \rightarrow oxazole), it is sometimes referred to as an ipso or isoheterocyclic rearrangement, but these terms are not appropriate. A ring-degenerate rearrangement is a better choice, and will be used. This situation may result in a (fully) degenerate rearrangement when the starting and final products are identical (with identical substitution patterns). In order to demonstrate their existence, deuterium labelled studies or variable temperature nmr analyses have been used.

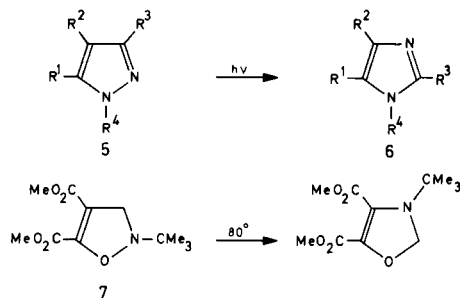
1. Rearrangements Involving No Side-Chain Atoms.

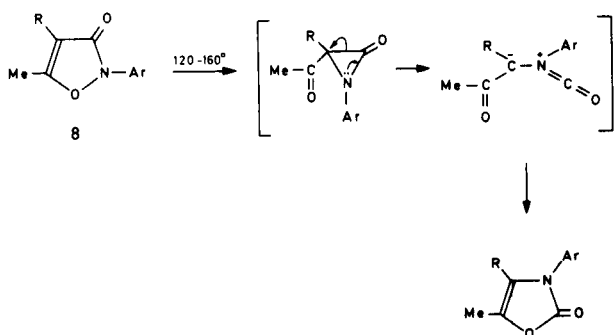
To this category belong all rearrangements which involve the interchange of annular atoms. They are best known in the field of isoxazoles **1** which are converted thermally (above 200°) or better photochemically, into oxazoles **4** [2]. The reactions occur by a ring contraction-ring expansion mechanism and proceed *via* acylazirines **2** which isomerize to nitrile ylides **3** and then ring close to oxazoles **4**. Although it is generally accepted that the ring contraction step involves a homolytic cleavage of the weak

O-N bond, a concerted mechanism for the thermal process has also been proposed [3]. In many cases, the azirines have been isolated and then converted into oxazoles under different conditions. For instance, irradiation of 3,5-diphenylisoxazole (**1**, R¹ = R³ = Ph, R² = H) in ether with 253.7 nm light and interruption of the reaction before completion led to the isolation of 3-benzoyl-2-phenyl-1-azirine [4]. This compound could be transformed into the corresponding oxazole by further irradiation with 253.7 nm light or converted back to the isoxazole with light > 334 nm.

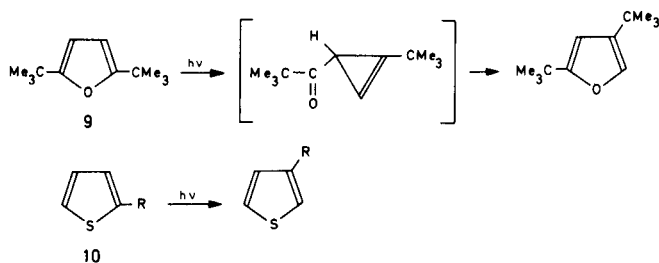


Rearrangements of this type are not limited to isoxazoles, but have also been reported for pyrazoles **5**, which isomerize to imidazoles **6** [5], and for non-aromatic rings [6,7] such as **7** and **8**. In the latter case, an α -lactam was postulated as an intermediate. Although not recognized so far, this highly unstable three-membered ring [8] probably isomerizes into a dipolar species before recyclization occurs.





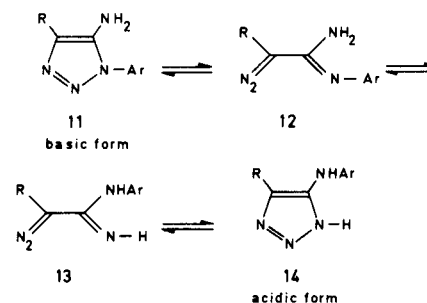
When only one heteroatom is present in the molecule (e.g. **9** and **10**), the rearrangement can be carried out photochemically and results in the interchange of the substituents at the 2- and 3-positions [9]. These are examples of ring-degenerate rearrangements which may proceed *via* cyclopropenes.



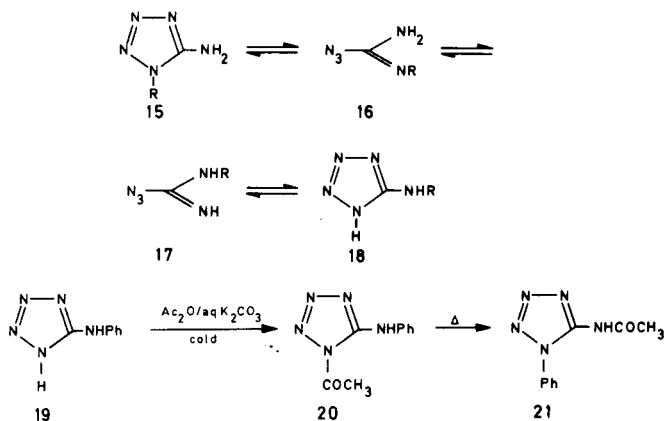
The photoisomerization of a number of five-membered ring heterocycles does not follow the ring contraction-ring expansion pathway. The subject has been reviewed recently by Padwa, and the reader is referred to this paper for further information [9].

2. Rearrangements Involving One Side-Chain Atom.

The exchange of an endocyclic with an adjacent exocyclic heteroatom is called the Dimroth rearrangement because it was first discovered by Dimroth in 1909 for the interconversion of 1-aryl-5-amino-1,2,3-triazoles **11** and 5-anilino-1,2,3-triazoles **14** [10]. The mechanism of this isomerization has been studied in detail [11]; and involves ring cleavage of **11** to a diazoimine **12**, followed by proton shift to **13** and recyclization to **14**. An equilibrium is reached in the molten phase ($R = Ph$) and its position is shifted towards the acidic isomer as the electronegativity of the Ar-substituent increases. The nature of the solvent also affects the equilibrium, favoring the acidic form in basic solvent (such as pyridine). Kinetic measurements have disclosed a linear relationship between the logarithms of the rate and equilibrium constants. Thus, the presence of electron-withdrawing groups at both the 1-position and the 4-position facilitates the forward reaction (**11** \rightarrow **14**) and retards the reverse reaction. In many cases the diazo-imines have been isolated as final products; e.g. from the ring-opening reactions of 1-sulfonyltriazoles containing a disubstituted amino group at the 5-position [12].



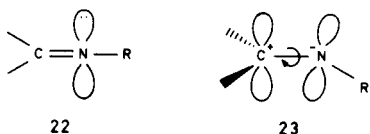
The isomerization of 1-alkyl and 1-aryl-5-aminotetrazoles **15** to 5-(substituted)aminotetrazoles **18**, or *vice versa*, at 180-200° is another example of a Dimroth-rearrangement which now proceeds *via* azido-imines (**16** and **17**) as intermediates [13]. The logarithms of the equilibrium constants are linearly correlated with the Hammett's σ -values for arylsubstituents, thus favoring the acidic form **18** for electron-withdrawing groups. This behaviour is nicely illustrated by the conversion of 1-acetyl-5-phenylaminotetrazole **20** into 1-phenyl-5-acetamidotetrazole **21** on heating in xylene [14]. Compound **20** was obtained by acetylation of 5-phenylaminotetrazole **19** under mild conditions. The same reaction sequence is reported for 5-benzylaminotetrazole (**19**, $PhCH_2$ instead of Ph).



Considerable attention has been focused recently on the mechanistic details of each individual step of the Dimroth rearrangement of **15**. The proton shift which occurs in going from **16** to **17** can only take place after *syn-anti* isomerization about the $C=N$ bond, since the electrocyclic ring opening of **15** yields **16** in the *E*-configuration. According to *ab initio* calculations, the rate determining step of the isomerization **15** \rightarrow **18** ($R = H$) in the vapor phase is not the ring-chain isomerization (**15** \rightarrow **16**), but either the *syn-anti* isomerization about the $C=N$ bond of **16** and **17**, or the 1,3-sigmatropic shift of the proton (**16** \rightarrow **17**) [15]. Since the unfavourable proton shift can be circumvented by a bimolecular process in the liquid phase or by using protic solvents, the *syn-anti* isomerization may be safely regarded as the rate-determining step under the usual ex-

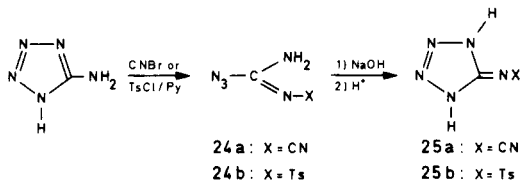
perimental conditions.

Two mechanisms for the *syn-anti* isomerization of imines and their derivatives have been proposed; an inversion or lateral shift mechanism by way of a linear transition state **22**, and a bond-rotation mechanism as shown in **23** [16]. The distinction between these two mechanisms has been the subject of much discussion, but it now appears that in most cases, except for protonated species, the inversion mechanism is operating. Electron-attracting R-substituents lower the energy barrier to inversion, and, consequently, enhance the rate of the Dimroth rearrangement.



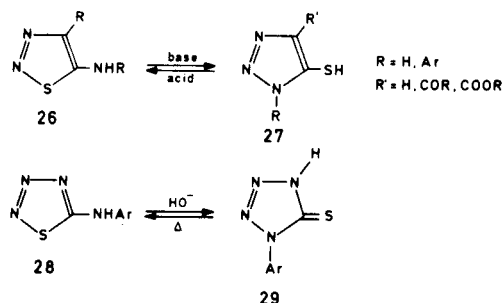
After the sequence of *syn-anti* isomerization, proton shift and a second *syn-anti* isomerization, ring closure to **18** can now occur by attack of the imine nitrogen lone-pair at the terminal nitrogen atom of the azide [17]. The transition state is reached when the azide system has bent to an angle of 136°. In the azide-tetrazole equilibrium, the tetrazole form is normally the predominant isomer, except when strong electron attracting R-groups (such as NO₂, CN, RSO₂) are present which stabilize the azide form. Higher temperatures, nonpolar solvents and acids also shift the equilibrium position towards the azide isomer [18]. Thus, there is a parallelism between the equilibrium constant for ring opening (**15** → **16**) and the rate of *syn-anti* isomerization of **16**.

Examples are known where the Dimroth rearrangement can be stopped at the stage of the open-chain azide isomer. Thus, the reaction of 5-aminotetrazole with cyanogen bromide or tosyl chloride leads to the stable guanyl azides **24a,b** [19]. Attack of the reagents occurs at the ring NH of the tetrazole, followed by decomposition. A base is required to effect the cyclization of **24a,b** into the tetrazoles **25a,b**. There is now general agreement that 5-cyanamino-tetrazole and 5-tosylaminotetrazole exist in their tautomeric imino-form **25** [20].

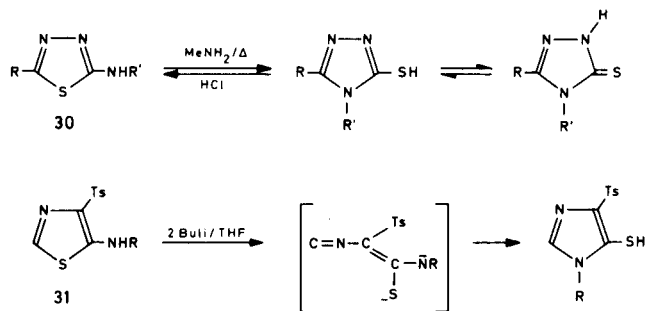


Closely related to the rearrangements of aminotriazoles and aminotetrazoles are the reversible isomerizations of 5-amino-1,2,3-thiadiazoles **26** into 5-mercapto-1,2,3-triazoles **27** and of 5-amino-1,2,3,4-thiadiazoles **28** into 1,2,3,4-tetrazolin-5-thiones **29** [21,22]. The forward reactions are base-catalyzed and initiated by proton abstraction, where-

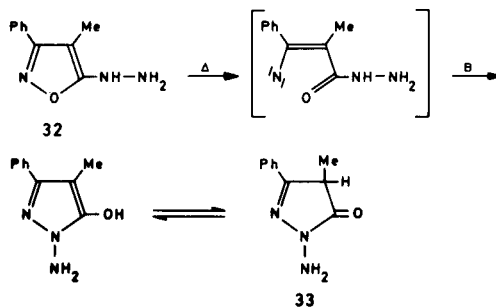
as the reverse reactions occur either in acidic media (for **27**) or in refluxing benzene (for **29**). The conversion **28** → **29** is promoted by the presence of electron-withdrawing aryl substituents, but even then the yields are low (not more than 37%) due to competitive degradation into isothiocyanate and azide ion. Note also that the 5-mercapto-tetrazole exists in the tautomeric thione structure **29** [23].



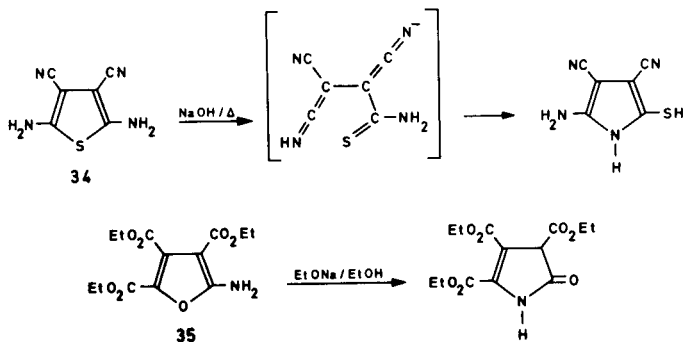
2-Amino-1,3,4-thiadiazoles (**30**) [24] and 4-tosyl-5-aminothiazoles (**31**) [25] are also capable of undergoing the Dimroth rearrangement under basic conditions. In the case of the 4-tosyl substituted thiazole **31**, two equivalents of butyllithium are necessary to deprotonate both the NH and C₂-H hydrogens before ring opening can occur. Recyclization then furnishes the imidazole after neutralization.



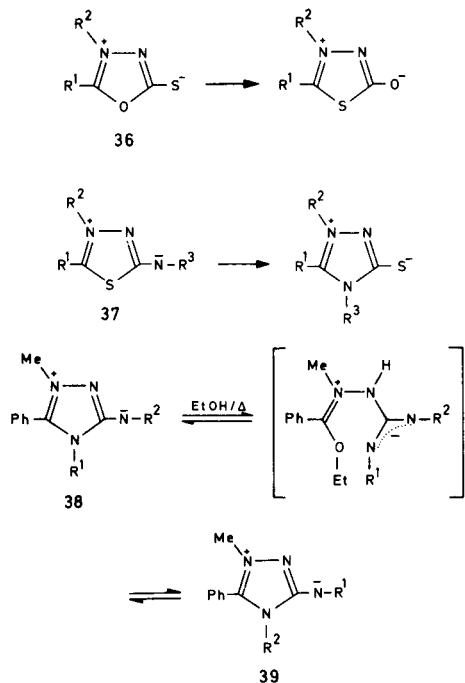
Thermally, and in the presence of a base such as hydrazine, 5-hydrazinoisoxazoles can be isomerized into 1-amino-pyrazolin-5-ones (e.g. **32** → **33**) [26]. This reaction is interpretable in terms of a vinyl nitrene intermediate resulting from O-N bond cleavage. Deprotonation and recyclization then furnish the rearranged product **33**. The observed Dimroth rearrangement is in contrast with the thermolysis of isoxazoles into oxazoles (**1** → **4**), and also with the thermal behaviour of 5-aminoisoxazoles (see **44** → **45**).



The “ π -excessive” aromatic heterocycles (furans, thiophenes, pyrroles) are not prone to undergo the Dimroth rearrangement, unless strong activating groups are present at the appropriate positions [27]. An interesting example is the base-induced isomerization of **34** into a pyrrole derivative by way of the indicated intermediate. The substituted aminofuran **35** undergoes a similar rearrangement.



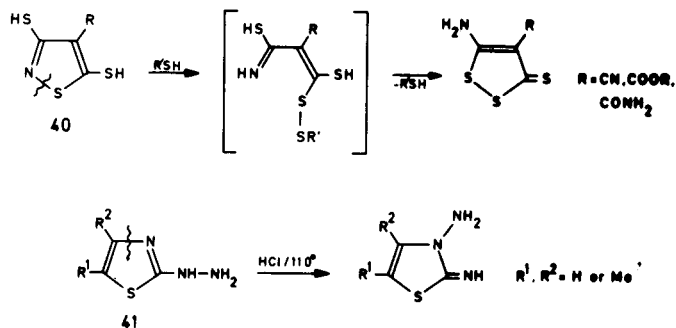
In the field of mesoionic compounds, several Dimroth rearrangements have been reported (e.g. **36-39**) [28]. They occur on heating in protic solvents, on heating with a base, or simply on heating. The interconversion of the mesoionic 1,2,4-triazolium-3-imines **38** and **39** is a case of ring-degenerate rearrangement. When R^1 and R^2 are respectively *p*-tolyl and phenyl, a 1:1 equilibrating mixture is obtained in boiling ethanol [29].



In all cases thus far discussed, the Dimroth rearrangement of the aromatic heterocycles involves the interchange of two heteroatoms which are singly bound to a common ring-carbon atom; i.e.:

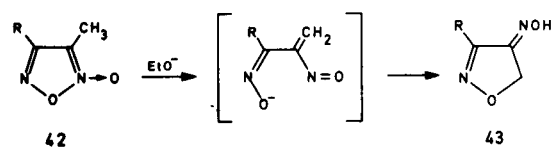


We have found only two exceptions to this general scheme, namely the isomerizations of **40** and **41**, where the azole C=N bond participates in the rearrangement [30]. It is noteworthy that the rearrangement of **40** occurs spontaneously when its disodium salt is acidified to neutralization. The reaction is assumed to be catalyzed by the presence of SH in the molecule.

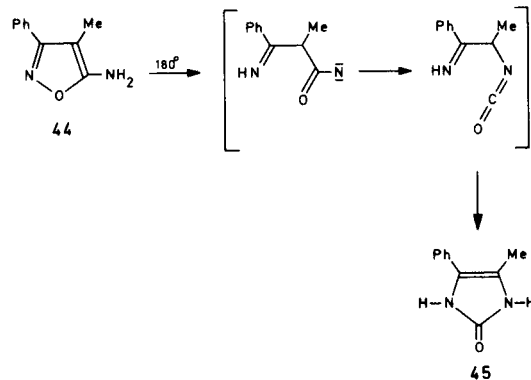


Finally, Dimroth rearrangements occur frequently and under mild reaction conditions with non-aromatic heterocycles, when exocyclic double bonds are present adjacent to a ring heteroatom. The reader is referred to the addendum for examples.

A reaction closely similar to the Dimroth rearrangement is Angeli's rearrangement of 3-methylfuroxans **42** into oxime derivatives of isoxazolin-4-ones **43** [31]. In this case, the participating side-chain atom is carbon instead of a heteroatom.

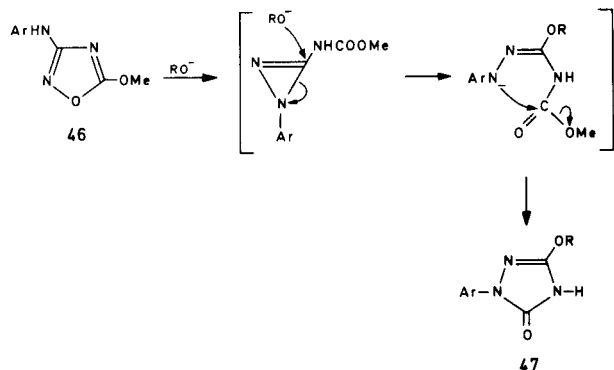


A few rearrangements involving one side-chain atom have been reported which definitely differ from the Dimroth rearrangement. For instance, when the aminoisoxazole **44** is heated at 180°, the isomeric imidazolin-2-



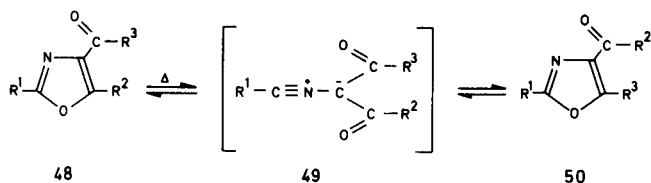
one **45** is obtained together with the expected azirine (*cf.* **1** → **2**) [32]. A plausible mechanism involves the generation of an acyl nitrene which rearranges to an isocyanate and then closes to give **45**. The mechanism, however, is questionable and needs further investigation.

Recently, Jones *et al.* [33] discovered the unusual transformation of the 1,2,4-oxadiazoles **46** into the 1,2,4-triazolin-3-ones **47** on treatment with alkoxide in refluxing alcohol. They proposed a mechanistic rationalization based on the intermediacy of an unstable diazirine. Since the methoxy function of the starting material is replaced by the alkoxide of the reacting base before recyclization occurs, this reaction cannot be considered as a true molecular rearrangement.

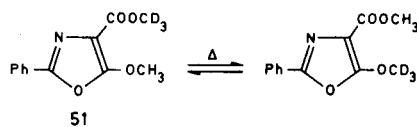


3. Rearrangements Involving Two Side-Chain Atoms.

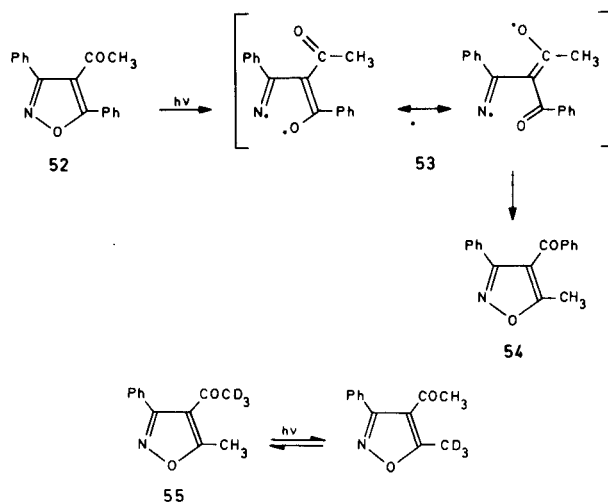
This class of rearrangements is scarcely documented in the aromatic field. The Cornforth rearrangement, discovered in 1949, belongs to this category and involves the thermal interconversion of 4-carbonyl substituted oxazoles **48** and **50** with dicarbonylnitrile ylides **49** as postulated intermediates [2a,34]. The nature of the substituents R^2 and R^3 determine whether the rearrangement occurs. For instance, 5-alkoxyoxazole-4-carboxamides (**48**, $R^2 = OR$, $R^3 = NR_2$) rearrange readily at 90-120° to 5-aminoxazole-4-carboxylates (**50**, $R^2 = OR$, $R^3 = NR_2$) in excellent yields [35].



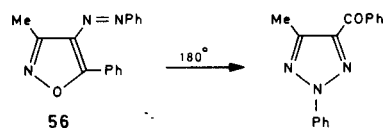
When the substituents R^2 and R^3 are identical, the Cornforth rearrangement is degenerate and leads to a 1:1 equilibrium mixture. This was demonstrated when the deuterium labelled oxazole **51** was heated at 95° [35].



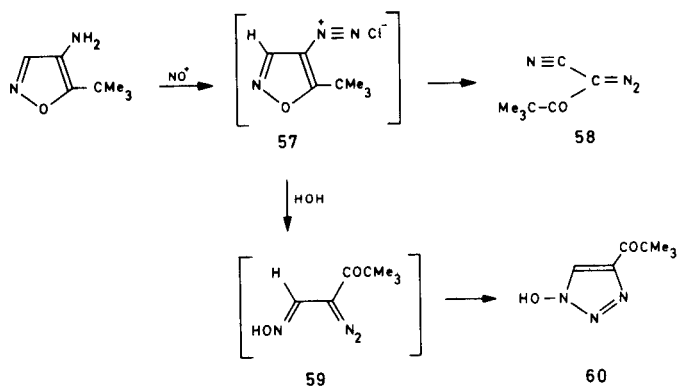
During the isomerization of 4-acylisoxazoles into 4-acyloxazoles (**1** → **4**, $R^2 = RCO$), rearrangement into isomeric isoxazoles has been observed [36]. Thus, irradiation of 3,5-diphenyl-4-acetylisoxazole **52** in benzene produces 3-phenyl-4-benzoyl-5-methylisoxazole **54** as the primary photoproduct. On further irradiation, this material rearranges to oxazole. Also, irradiation of 4-trideuterioacetyl-5-methyl-3-phenylisoxazole **55** results in scrambling of the deuteriomethyl group (degenerate rearrangement). The results are easily rationalized in terms of O-N bond cleavage to a resonance-stabilized diradical intermediate **53** which recloses to product.



A similar reaction was reported by Wittig and co-workers [37] in 1928 for the thermolysis of the 4-phenylazoisoxazole **56** into a triazole.

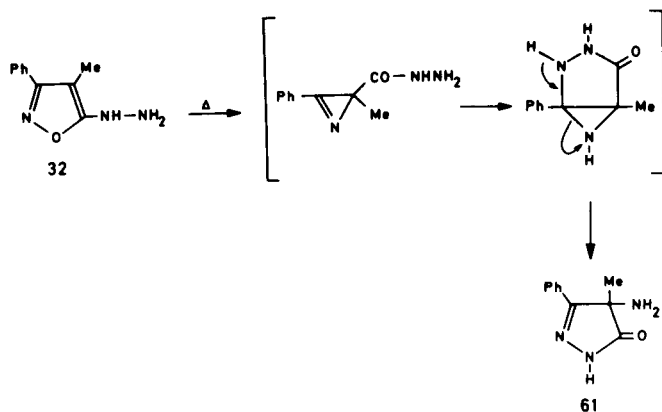


Finally, we have observed an example of spontaneous rearrangement during the generation of the diazonium salt **57** derived from 4-amino-5-*t*-butylisoxazole [38]. The decomposition products were found to be the α -cyanodi-azoketone **58** (44%) and the rearranged triazole **60**



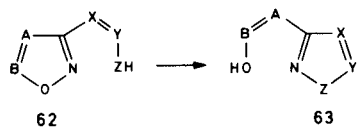
(35.5%). The diazo compound **58** obviously results from deprotonation and ring cleavage of **57**, whereas the formation of **60** is accounted for by cyclization of the diazo-oxime **59**, which would result from **57** by hydrolysis.

In all the previous reactions two side-chain atoms from the 4-position of the heterocycle are involved in the rearrangement. A unique case with involvement of two side-chain atoms from the 5-position is the thermal isomerization of some 5-hydrazinoisoxazoles into 4-aminopyrazolin-5-ones, exemplified for **32** → **61** [26]. The reaction most probably proceeds *via* an azirine and bicyclic compound as intermediates. This pathway competes with the Dimroth rearrangement **32** → **33**, and the ratio of products depends on the nature of the solvent used. Substitution at the hydrazine moiety of **32** also affects the product distribution.

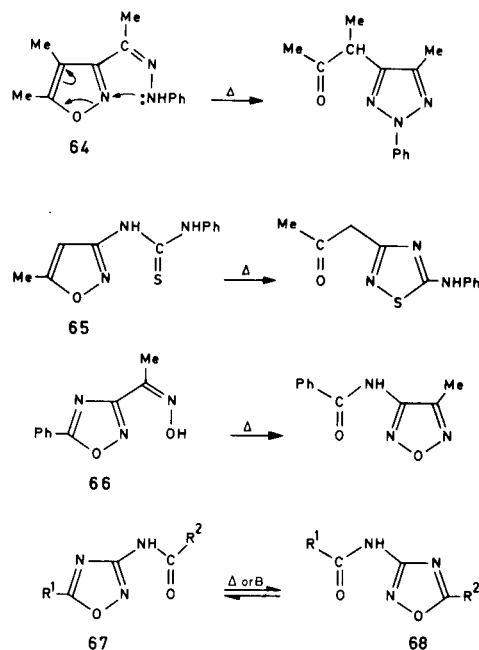


4. Rearrangements Involving Three Side-Chain Atoms.

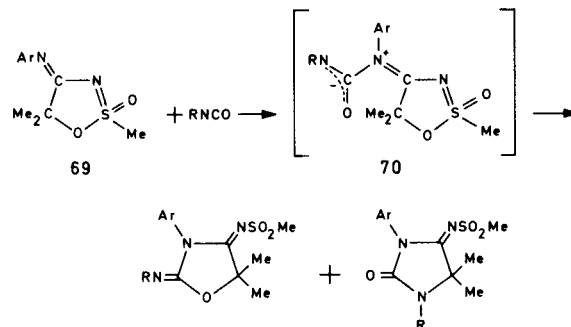
In 1967, Katritzky and co-workers [39] generalized a series of known and new rearrangements in a consistent picture, **62** → **63**, which is now referred to as the Boulton-Katritzky scheme. The designation "mononuclear heterocyclic rearrangement", used by several authors and also in a recent review article [40], is inadequate because it does not delineate the scope of the rearrangement. The Boulton-Katritzky scheme includes azole-azole interconversions, and is limited to heterocycles containing the N-O bond; *i.e.* isoxazoles, 1,2,4-oxadiazoles and 1,2,5-oxadiazoles. The nucleophilic C-3 substituent (XYZ) is a heteroallyl moiety, although it has been extended recently to saturated chains [41]. As expected for an S_Ni -type reaction, the reactivity depends on the nucleophilicity of the side chain, and for a given side chain, the tendency to rearrange decreases in the order 1,2,4-oxadiazoles > isoxazoles > 1,2,5-oxadiazoles. Usually, the reactions occur on heating with or without a base, sometimes in the presence of copper powder.



The scope of the Boulton-Katritzky scheme has not yet been fully exploited, and new reactions are frequently reported [42]. A few typical examples (**64**–**67**) are given below. The thermal interconversion of the 1,2,4-oxadiazoles **67** and **68** is the only known example of a reversible process [43]. For $R^1 = \text{Me}$ and $R^2 = \text{Ph}$, equilibrium is reached at room temperature in solution, particularly in a dipolar aprotic solvent such as DMSO, or rapidly on brief heating at 180°. The reaction is also catalyzed by addition of a base (*t*-BuOK). When both R^1 and R^2 in **67** are methyl substituents, the potassium salt exhibits a degenerate rearrangement at 112°, as shown by the coalescence of the methyl signals in the nmr spectrum (DMSO as solvent).

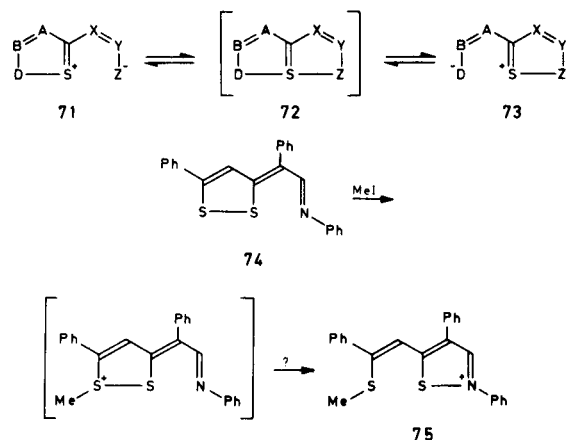


An interesting reaction which bears some analogy with the Boulton-Katritzky scheme, is the cycloaddition of 4-imino-4,5-dihydro-1,2λ⁶-3-oxathiazol-2-ones **69** with heterocumulenes, exemplified below for isocyanates [44]. Here, the dipolar intermediate **70** is postulated in order to rationalize the formation of the products.

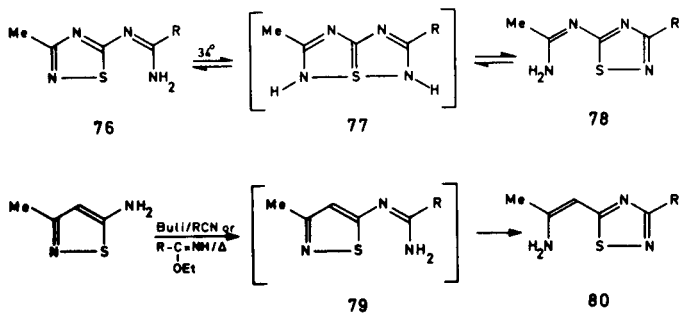


When the pivotal nitrogen atom in the Boulton-Katritzky scheme is replaced by sulfur, *i.e.* **71** → **73**, we are at the borderline of no-bond resonance. Indeed, **71**

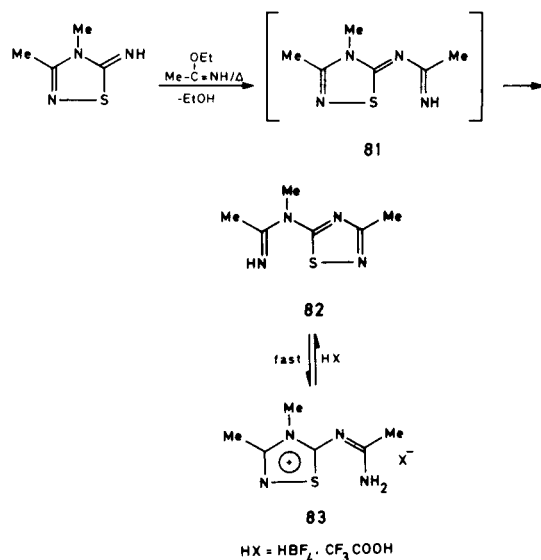
and **73** also represent the canonical forms of a 1,6-dihetero- $6\lambda^4$ -thiapentalene **72**. Hence, in a number of examples it is difficult to establish that a reaction is taking place at all, rather than that the two sides of the equation represent canonical forms of a molecule of intermediate structure. For instance, methylation of the dithiole **74** occurs at sulfur with formation of an isothiazolium salt **75**. Here, the problem of rearrangement *versus* mesomerism is an open question [45].



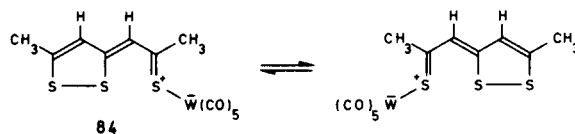
Some clear-cut rearrangements with displacement at sulfur have been described by Akiba *et al.* [46]. Thus, the 1,2,4-thiadiazoles **76**, bearing an amidino substituent at the 5-position, may exist in equilibrium with the isomeric structures **78**. The reaction is described as proceeding through the thiapentalene **77** with a linear N-S-N group. The equilibrium position is dependent on the solvent, the temperature and the nature of the R-substituent, bulky groups and electron-withdrawing substituents favoring **78**. Similarly, during the preparation of the isothiazoles **79**, the isomeric 1,2,4-thiadiazoles **80** were obtained as the most stable reaction products.



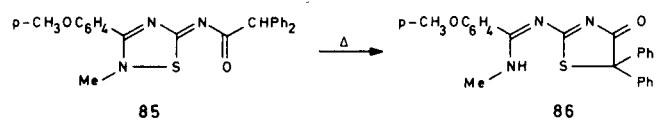
Akiba *et al.* also reported a reaction sequence with two rearrangements; the first occurring during the preparation of **81** where the isomer **82** is obtained, and the second when **82** is transformed into the salt **83** [47].



A beautiful example of a degenerate rearrangement has been reported by Reid *et al.* for the pentacarbonyltungsten(O) complex of 1,6,6a λ^4 -trithiapentalene [48]. Thus, **84** displays fluxional behaviour in chloroform solution. At -20° , the nmr spectrum shows two sharp ring signals and two sharp methyl signals which coalesce at 1° and 4° respectively. At 33° , the two isomers are rapidly interconverting on the nmr time scale.

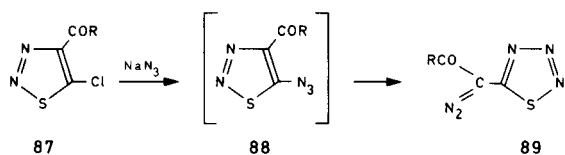


We have also observed a number of rearrangements during our research in the thiapentalene field. One selected example is the isomerization of **85** into **86** on heating in a polar solvent [49].

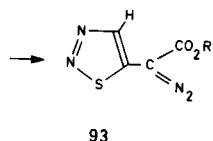
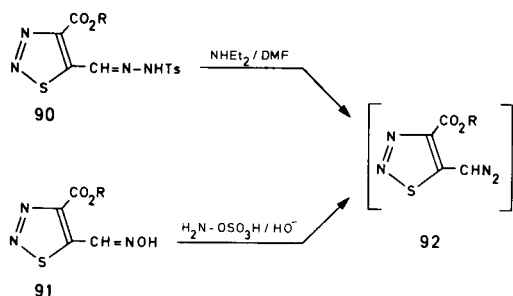


Recently, a novel class of rearrangements has been discovered [50] which bears some analogy both with the bond-switch rearrangements at sulfur discussed above and with the Dimroth rearrangement. Thus, when the 5-chloro-1,2,3-thiadiazoles **87** were treated with sodium azide under the conditions normally used to prepare the azides **88**, a spontaneous isomerization occurred with formation of the diazoalkyl substituted 1,2,3,4-thiatriazoles **89**. The same behaviour was observed when the azide function is replaced by a diazomethyl function, in which case a rearranged 1,2,3-thiadiazole **93** is obtained. The diazomethyl substituted thiadiazole **92** was generated *in situ* from the corresponding tosylhydrazone **90** by the Bamford-Stevens reaction, or from the oxime **91** by the Forster reaction.

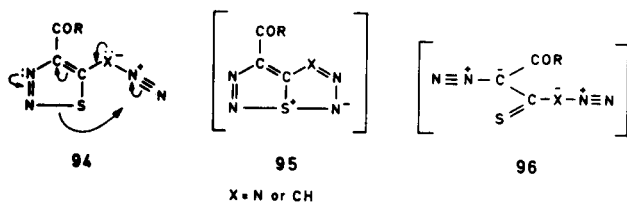
Under the basic conditions of the latter, saponification of the ester also occurred ($R = H$).



$R = Ph, OEt$

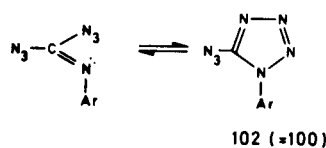
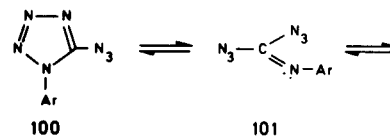
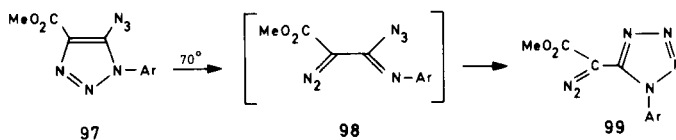


Mechanistically, the formation of **89** and **93** can be explained by a bond-switch process as shown in **94** for a concerted reaction, or possibly *via* the intermediacy of **95**. Since sulfur is the nucleophilic center in this process, the mechanism is basically different from that described in Akiba's work [46,47]. An alternative mechanism involves ring opening of the starting materials to give **96** in which the thioketone function is flanked by two 1,3-dipoles. Recyclization then occurs in the direction of the most stable isomer. The stabilizing effect of the carbonyl function on the diazomethyl substituent is the driving force of the rearrangement.



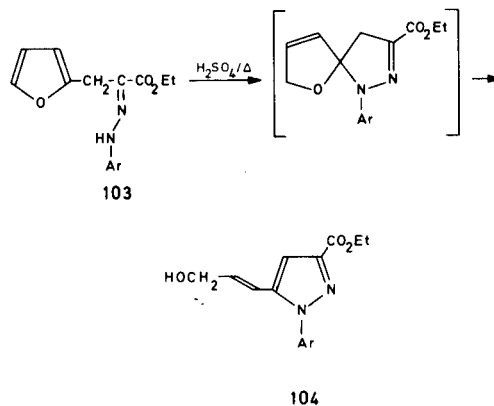
This type of rearrangement is not restricted to 1,2,3-thiadiazoles, but also occurs with 1,2,3-triazoles as illustrated for the thermal isomerization of **97** to **99** [51]. Here, the azidotriazoles **97** can be isolated and characterized as such. In view of the rather facile ring opening of triazoles into diazo-imines, as discussed above for the Dimroth rearrangement, **98** may safely be regarded as the intermediate. In this context, it is interesting to consider the reported equilibrium between the azidotetrazole **100** and the imino-bisazide **101** [22b]. If the energy barrier to rotation about the $C=N$ bond in **101** can be overcome during the

process, this would be a typical example of a degenerate rearrangement in going from **100** to **102**.



5. Rearrangement Involving Four Side-Chain Atoms.

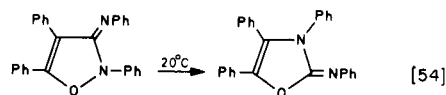
This field has not yet been developed. In fact, we have found only one example in the aromatic series, namely the isomerization of the arylhydrazone **103** to the pyrazole **104**, when subjected to the conditions used for indole synthesis [52]. This unexpected reaction presumably occurs by protonation of the furan ring and formation of a spiro intermediate which then rearranges.



6. Conclusions.

Two general conclusions are apparent from this review:

(i) The Dimroth rearrangement, involving one side-chain heteroatom, is the most frequently observed rearrangement in heterocyclic chemistry. It is not limited to five-membered ring systems and occurs as well with aromatic as with non-aromatic compounds. The reactions are either thermally induced or initiated by acids or bases.

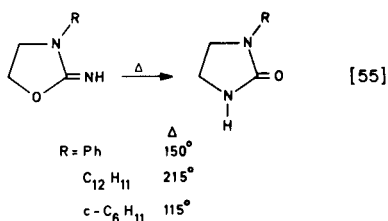


(ii) The isoxazole ring undoubtedly gives the largest variety of rearrangements. Indeed, isoxazoles have not only been isomerized to many other five-membered heterocycles, but also to azirines by ring contraction and to six-membered rings by ring expansion [53]. The facility of their rearrangement is due to the very weak O-N bond which is broken during the process. The outcome of the reaction depends mainly on the substitution pattern, and to a lesser degree on the reaction conditions.

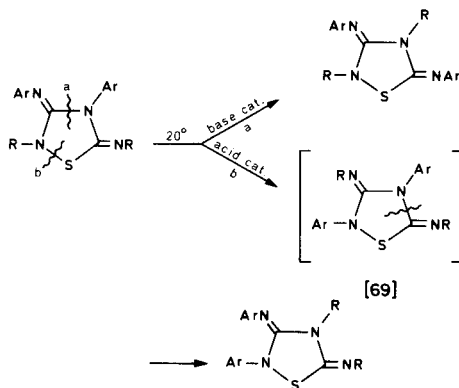
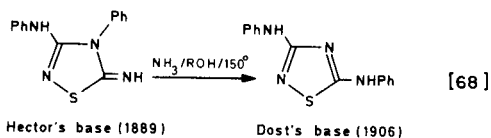
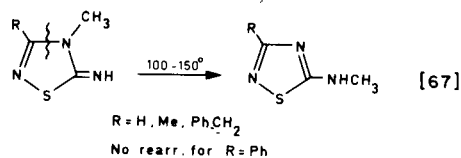
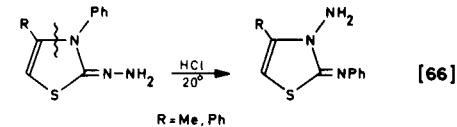
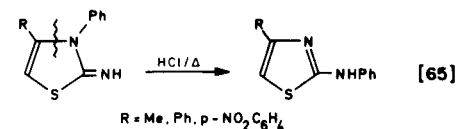
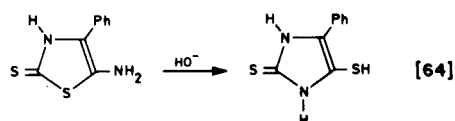
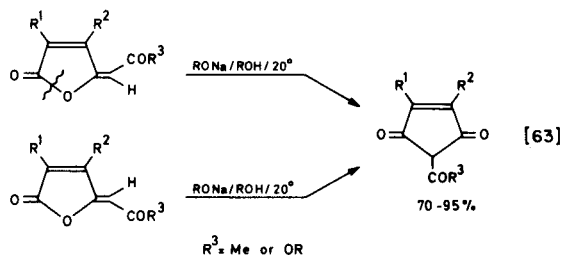
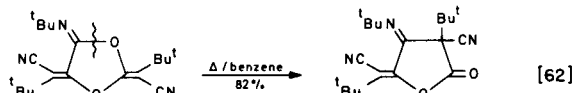
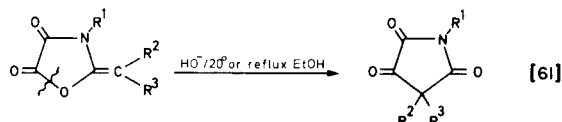
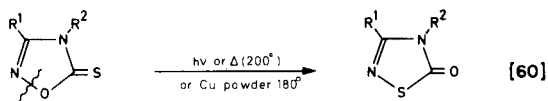
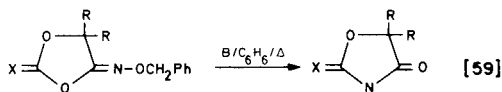
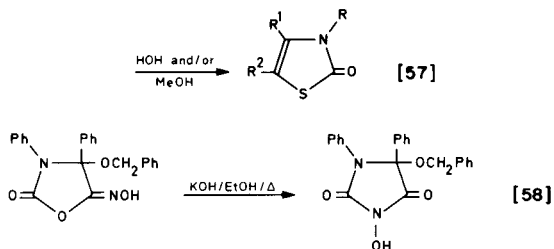
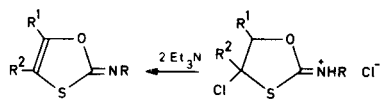
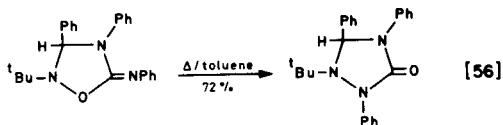
7. Addendum.

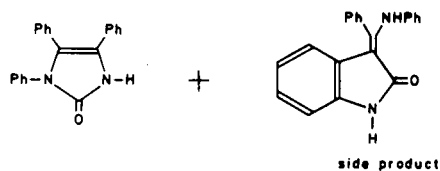
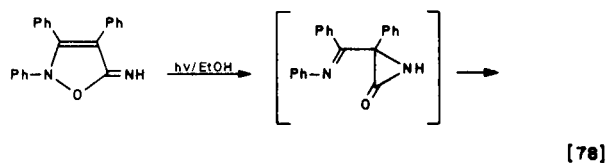
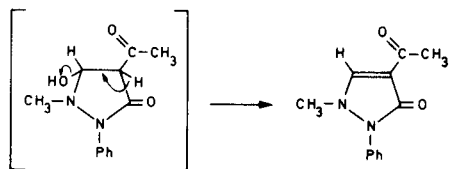
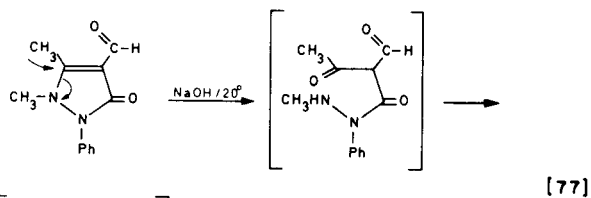
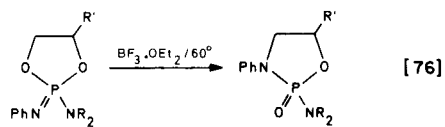
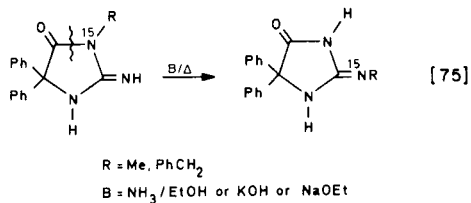
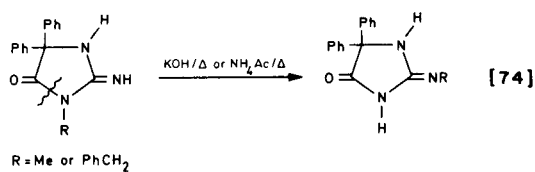
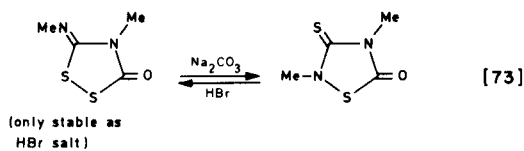
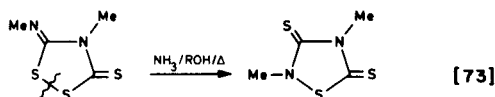
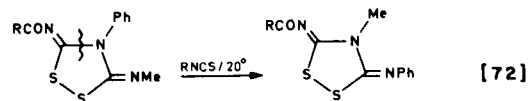
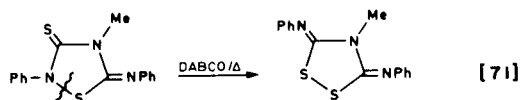
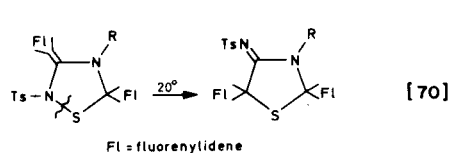
In this review, I have focused mainly on rearrangements which occur with aromatic heteromonocycles. The examples known to the author in the non-aromatic field are summarized below for the benefit of the reader.

a) Thermal Rearrangements Involving No Side-Chain Atoms.

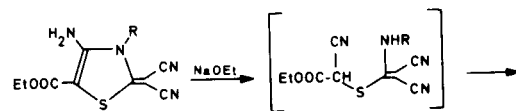
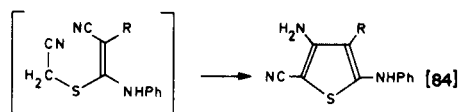
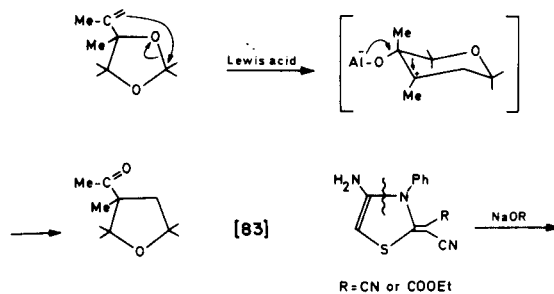
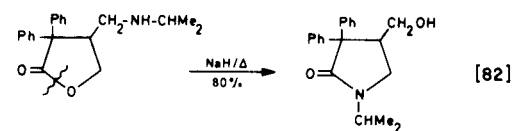
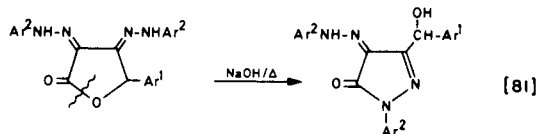
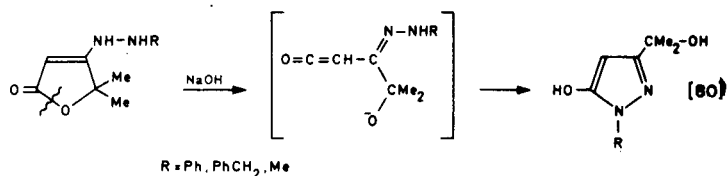
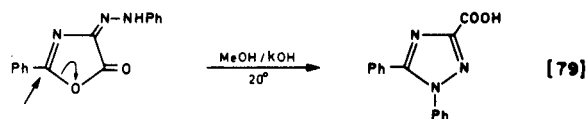


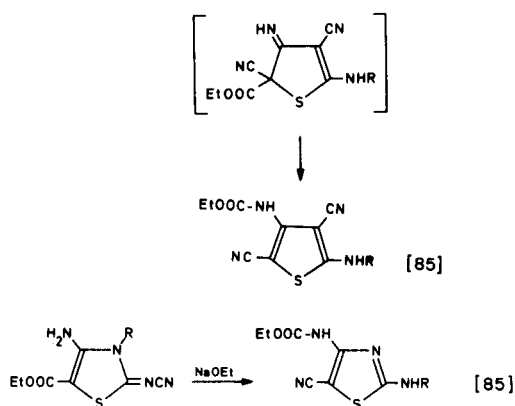
b) Rearrangements Involving One Side-Chain Atom.



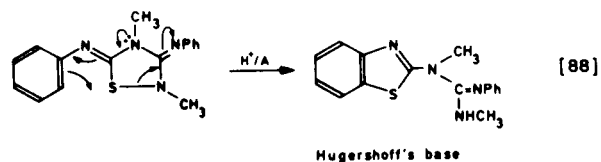
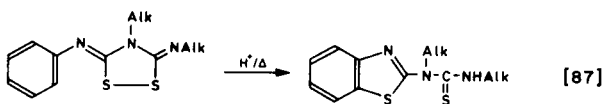
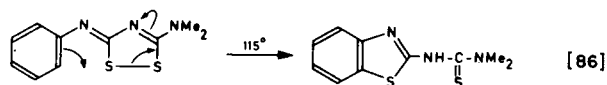


c) Rearrangements Involving Two Side-Chain Atoms.

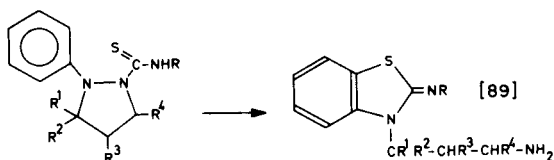




d) Rearrangements Involving Three Side-Chain Atoms.



e) Rearrangements Involving Four Side-Chain Atoms.



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