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Review Article

Ring Transformations in Tetrazole Chemistry

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Dedicated to Professor A. R. Katritzky on the Occasion of his 70th Birthday

Abstract. Transformations of heterocycles into tetrazoles as well as conversions of the latter into other rings are reviewed. The literature is covered through early 1998 (material that has been surveyed by Van der Plas [1] and Benson [2] is resumed in abridged fashion). From the wide variety of interconversions accumulated in this overview a great many processes emerge that are of prime importance preparatively; moreover, quite a number of reactions will arouse interest in their mechanisms.

1 Introduction

Regarding the wealth of ring interconversions observed with azapyrrole-type azoles, the class of tetrazoles reigns supreme because of the unique diversity of processes. This article aims to summarize the vast literature, with inclusion of work on tetrazole-yielding transformations. Findings that have already been surveyed in the monograph of Van der Plas [1] – the sole specific review until now – or in the preceding treatise of Benson [2] are referred to only indirectly (by citing the relevant page numbers of [1] and [2] within the captions to single chapters). Pertinent material has also been dealt with in the major general reviews and updates of tetrazole chemistry [3–7]; in these cases treatment of the subject is selective, with concepts that partly differ. The same holds for the specialized accounts on ring-fused tetrazoles [8], 1,5-dipolar cyclizations [9], thermolysis of tetrazoles [10] and intramolecular reactions of carbenes and nitrenes [11a].

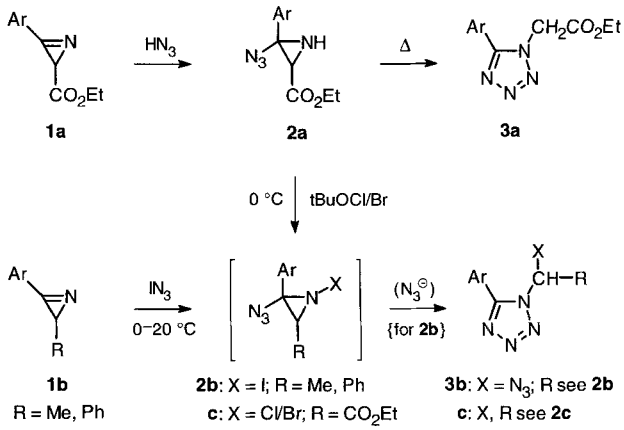
For practical purposes, presentation of material in this review is organized according to starting or produced rings rather than to reaction modes (the number of which amounts to about 30 in Section 2 and exceeds 40 in Section 3!). Ring transformations are commonly looked at as reactions that can be achieved in a one-pot procedure; however, because of their preparative importance processes that go through an isolable intermediate prior to giving the new ring will be treated as well. Yet, transformations of tetrazoloazines that *via* nitrene–carbene interconversions produce ring-contracted or -expanded derivatives of the initial azine moiety – a field thoroughly studied by Wentrup [11b,c] – are considered to fall outside the scope of the present survey; the same applies to azepine-forming reactions of (het)arylnitrenes and -carbenes that are generated from monocyclic tetrazoles [11a,b,d].

2 Tetrazoles obtained from other rings

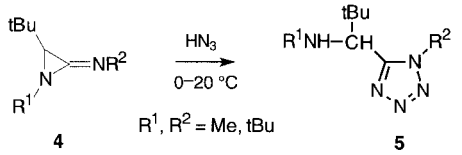
2.1 Three- and four-membered rings

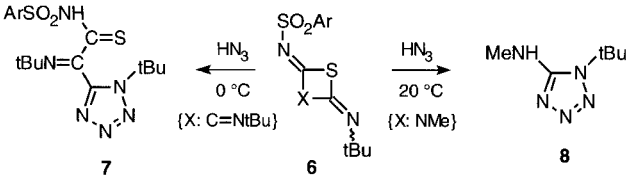
2H-Azirines, Aziridines, Thietanes, 1,3-Thiazetidines

2*H*-Azirines such as **1a,b** smoothly add hydrogen azide and iodine azide, respectively. The resultant azidoaziridine **2b** rapidly ring-opens (with loss of iodide ion) to



give, after uptake of unconsumed azide ion, the tetrazole **3b** [12]. Compound **2a** is stable, but on thermolysis at 80–100 °C it affords **3a** (besides molecular nitrogen, arenecarbonitrile and resinous material) [13a]. When **2a** is treated with hypohalogenite, tetrazoles of type **3c** are obtained directly in excellent yield; their formation proceeds *via* **2c**, which is detectable at −60 °C [13b]. Ring opening of the aziridinimine **4** with hydrogen azide leads to the 5-(aminoalkyl)tetrazoles **5** virtually quantitatively [14]. The same kind of azidolysis converts the four-membered rings **6** into the tetrazoles **7** [15] and **8** [16] in moderate to good yields. Product **8** is accompanied by a 1,2,3,4-thiatriazole which arises from addition of hydrogen azide to the arylsulfonyl isothiocyanate liberated during the main reaction. Remarkably, treatment of **6** (X = C=N-*t*-Bu, Ar = Ph) with sodium azide in DMF does not produce a tetrazole [15].





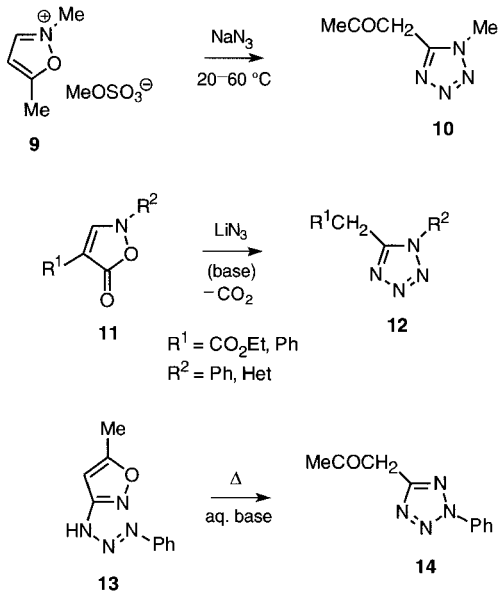
2.2 Five-membered rings with one or two heteroatoms

Benzofurans (p. 22 in [2]), *Isobenzofurans* (p. 24 in [2])

Azidolysis of the imidate moiety in 3-(phenylimino)isobenzofuran-1(3*H*)-one (*N*-phenylphthalisoimide) to give the respective *o*-(tetrazol-5-yl)benzoic acid is feasible not only by employing a chloroformic solution of hydrogen azide in a pressure bulb [2], but it can also be effected with sodium azide at low pH in an aqueous medium [17]; *N*-phenylphthalimide occurs as a side product the proportion of which increases with rising pH. – No new material is available on benzofurans.

Isoxazoles (p. 312 in [1]; pp. 24, 35 in [2]), *1,2-Benzisoxazoles* (p. 312 in [1])

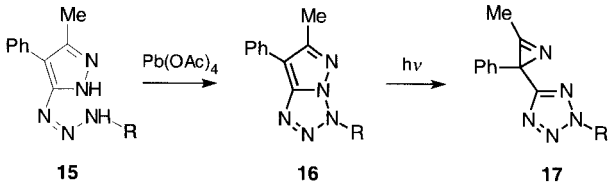
The important direct method to make 1-methyl-5-phenacyltetrazole by reacting a 2-methyl-5-phenylis-oxazolium salt with sodium azide [1] (see also [18]) has been extended to synthesize the acetonyl analogue **10** from **9** in good yield [19]. New information is also available on the reaction of 3-unsubstituted isoxazol-5(2*H*)-ones



11 with azide ion, showing that replacement of aqueous sodium azide [2] (see, in addition, [20a]) with lithium azide in THF gives far better yields of **12** (suppression of side products that arise from action of hydroxide ion) [20b]. With substrates like **11** (R^1, R^2 = Ph) the transformation proceeds only in the presence of a strong base [20b]. The Boulton-Katritzky rearrangement [21] of certain 3-triazenoisoxazoles into 2-substituted 5-acetonyltetrazoles [1, 2] is also applicable to the derivative **13**; preparation of the latter, however, requires a reverse protocol (*i.e.*, reaction of isoxazolediazonium ion with aniline); attempts to obtain **14** (Me in place of Ph) by the same procedure failed [22]. No new report has appeared on 1,2-benzisoxazoles.

Pyrazoles

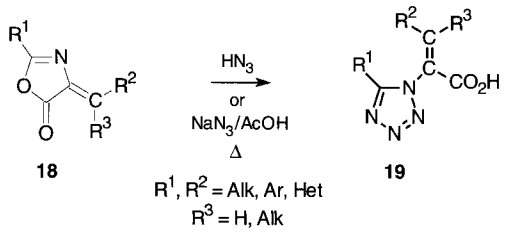
As regards tetrazole formation from a pyrazole, the only example known consists in the oxidative cyclization of the triazene **15** to the azapentalenic species **16** followed by UV irradiation to give **17** [23].



R = Alk, Ar

Oxazoles (p. 312 in [1]; p. 23 in [2])

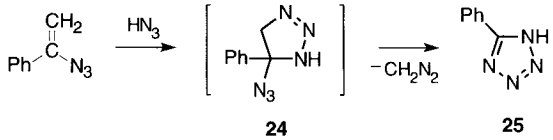
The long-known azidolysis of 4-ylideneoxazol-5(4*H*)-ones **18** [1, 2] has become the method of choice for making 2-(tetrazol-1-yl)alk-2-enoic acids **19** [24–26]; limitations can occur when both R^2 and R^3 are alkyl ligands [24].

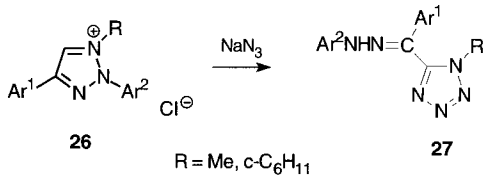


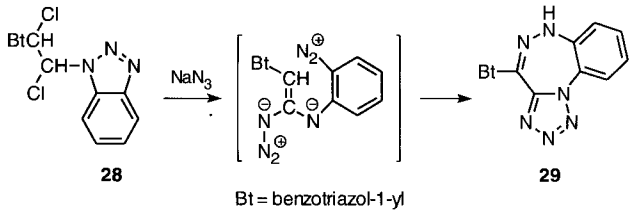
2.3 Five-membered rings with three or more heteroatoms

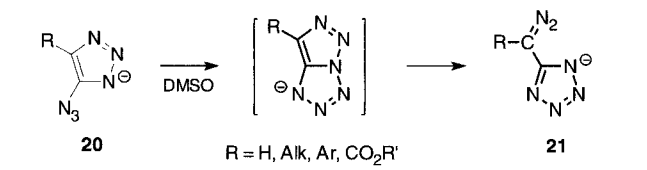
1H-1,2,3-Triazoles (pp. 354, 360 in [1]; p. 35 in [2])

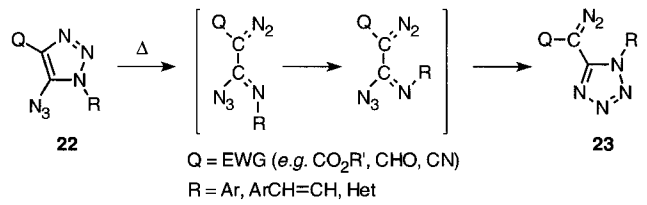
The anions **20**, generated from the respective tetrazoles with sodium hydride, rearrange at room temperature to the (α-diazoalkyl)tetrazolides **21** (half-life in DMSO at 32 °C: 0.75–2.5 hours); with derivatives **20** where R = acyl or CN, extensive decomposition occurs [27]. In a process mechanistically different from the foregoing reaction, the triazoles **22** on being heated to 60–80 °C isomerize to the tetrazoles **23**. This interconversion requires electron-withdrawing groups at C(4) [CO_2R, CHO, CH=NR, CN and others] and is enhanced by conjugated acceptor ligands at N(1) [28–30]; owing to the diazoalkyl side chain, certain tetrazoles **23** (EWG = SO_2Ph, CH=NR) can be obtained in derivatized form only [29]. The exhaustive study which beyond substituent effects includes kinetics and the influence of solvents has been briefly summarized elsewhere [31]. A rather unexpected transformation occurs when α-azidostyrene is heated with sodium azide and acetic acid in DMF: the resultant cycloadduct **24** does not react into 5-phenyl-1*H*-1,2,3-triazole but stabilizes through elimination of diazomethane to give the tetrazole **25** in low yield [32]. A net result as observed in the case **9** → **10** and **11** → **12** arises from ring cleavage of the triazolium ions in **26** with azide ion; **27** is obtained in fair yield (separation of (*E*)- and (*Z*)-isomers causes loss of material); with R becoming bulkier, the reaction rate increases [33]. Novel features regarding opening of the







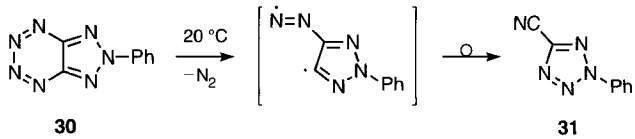




starting heterocycle as well as the overall structure of the transformation product are encountered when **28** is treated with sodium azide in DMSO at room temperature; **29** is isolated in over 60% yield [34]. For a mechanistic comment on the long-known thermolysis of 4-arylazo-1*H*-1,2,3-triazol-5-ols into 2*H*-tetrazole-5-carboxamides [1, 2], see [35].

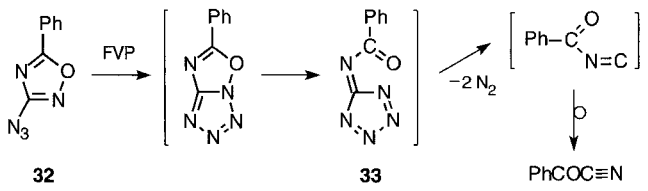
2H-1,2,3-Triazoles

A peculiar degradation reaction occurs when the bicycle **30** is kept in dichloromethane or chloroform: besides 2-phenyl-2*H*-1,2,3-triazole the tetrazole **31** is formed; the ratio of these two products depends on the solvent and reveals a first-order isotope effect on employment of $CDCl_3$ [36]. The interesting reaction has also been studied theoretically [37].



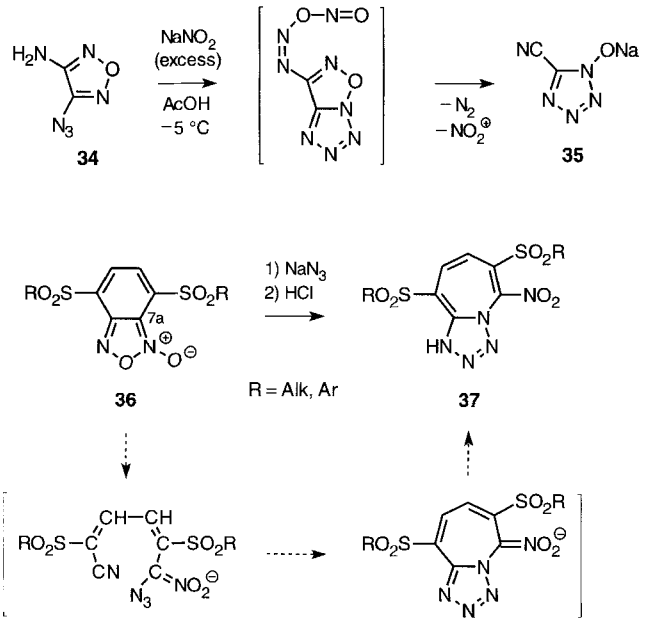
1,2,4-Oxadiazoles

Flash vacuum pyrolysis of the oxadiazolyl azide **32** leads to benzoyl cyanide. The transformation is thought to go through the unstable 5*H*-tetrazole **33**; this species, by loss of nitrogen, gives benzoyl isocyanide which isomerizes to the product [38].



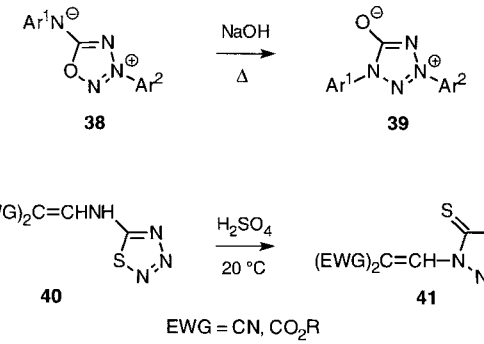
1,2,5-Oxadiazoles

An attempt to perform the Boulton-Katritzky rearrangement [21] with triazeno-1,2,5-oxadiazoles (*i.e.*, a class functionalized like **13**) failed: the expected 2*H*-tetrazol-5-yl ketone oximes could not be obtained [39]. A rather unusual transformation takes place when the oxadiazolamine **34** is treated with excess sodium nitrite in acetic acid. Remarkably, the proposed bicyclic intermediate ring-opens between position 5 and 6 to afford the sodium salt of the hydroxytetrazole **35** (ca. 50% yield) [40]. 1*H*-Tetrazolo[1,5-*a*]azepines **37** are formed in reasonable yield upon treatment of the benzofuroxans **36** with sodium azide in DMF and acidic work-up (the depicted tautomeric form is favoured by the acceptor ligands of the azepine unit). The compounds are likely to arise from attack of the azide ion at C(7a) followed by cleavage of the O–N(3) bond and an intramolecular azide to nitrile cycloaddition [41].



1,2,3,4-Oxatriazoles

The mesoionic derivatives **38** undergo a Dimroth rearrangement to the tetrazolium-5-olates **39** on being heated with ethanolic sodium hydroxide [42]. The early workers [42a] thought of the products as having a bridged structure, the correct one was established not until 1964 [43]. Compounds **38** bearing alkyl [44a] as well as H or NO ligands [44b] in place of Ar^1 are not candidates for this kind of ring transformation. Failure is also reported for thio analogues of **38** [45].



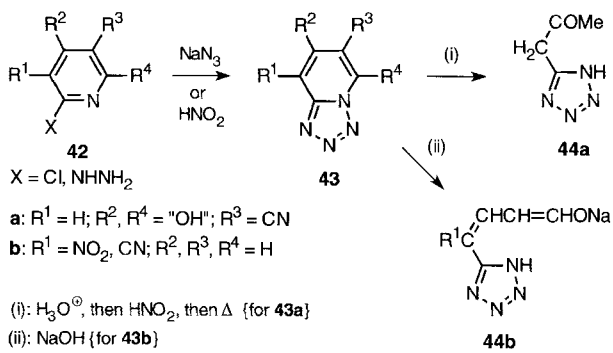
1,2,3,4-Thiatriazoles (p. 413 in [1]; p. 19 in [2]), *1,2,3,5-Thiatriazoles* (p. 414 in [1]; p. 24 in [2])

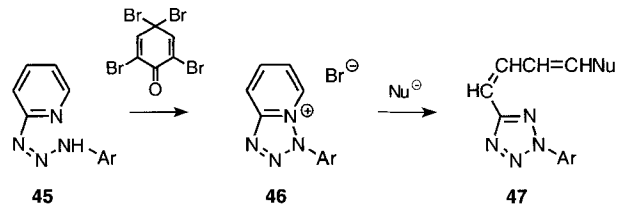
The well-studied rearrangement of 5-(arylamino)-1,2,3,4-thiatriazoles into 1*H*-tetrazole-5(4*H*)-thiones, effected with aqueous base, continues to find preparative application (see for example [46]). Interestingly, also solid barium hydroxide or strontium metal suspended in toluene containing HMPA brings about this transformation as recently shown for a naphthylamino derivative [47], and thiatriazoles like **40** give the tetrazoles **41** in reasonable yield under acidic conditions [48]. – No new material is available on 1,2,3,5-thiatriazoles.

2.4 Six-membered rings with one or two heteroatoms

Pyridines, Quinolines (p. 53 in [2]), *Isoquinolines*

The polyfunctionalized pyridine **42a** (X = $NHNH_2$) is readily transformed into the bicycle **43a** (of both compounds, tautomers different from those depicted may be involved) which on stepwise hydrolysis and decarboxylation affords the acetonyltetrazole **44a** in moderate yield [49]. Under the influence of bases tetrazolopyri-



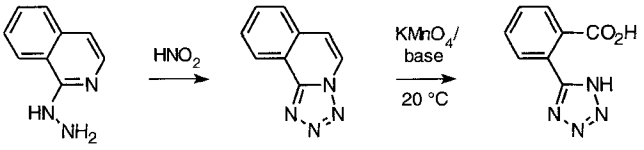


45 46 47

Nu = H, D, Me, CN, (OH), OR, NR_2, SR

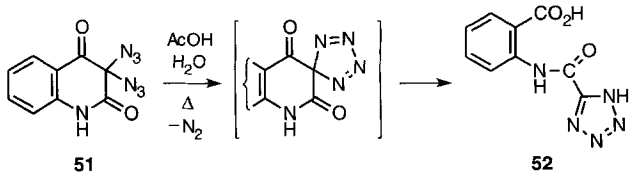
dines such as **43b** (obtained from **42b** having X = Cl) ring-open to the sodium dienolates **44b** whose stereochemistry has been studied; the reaction also works with a 6-nitro derivative **43** ($R^3 = NO_2$; R^1, R^2, R^4 = H) [50].

A very useful method for making 2*H*-tetrazoles **47** bearing a (functionalized) buta-1,3-diene chain at C(5) consists in oxidative ring closure of the triazenopyridine **45** followed by cleavage of the heteroaromatic cation of **46** with a nucleophile [51]. In certain cases ambident behaviour is observed. For instance, methoxide ion attacks **46** also at the bridgehead carbon atom, thereby giving rise to 1-(arylamino)pyridin-2(1*H*)-ones – a reaction course that predominates with angularly benzofused congeners of **46** [52a] but, in accordance with FMO theory, does not occur with linearly fused analogues [52b]. A brief summary of these reactions which have also been studied in stereoelectronic respect [51b, d] is available [53].



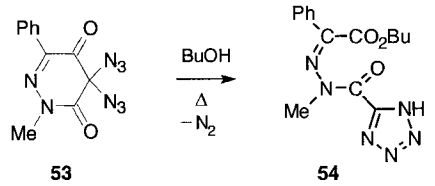
48 49 50

Oxidative degradation of the pyridine unit in compound **49** which is obtained from the isoquinoline **48** affords the tetrazolyl-substituted benzoic acid **50** in fair yield [54]. Another example for the long-known oxidation of the tetrazolo[1,8]naphthyridine system to the parent tetrazole [2] is shown in ref. [55]. According to a recent finding the *gem*-diazido derivative **51** can be used as a source for the specially substituted tetrazole-5-carboxamide **52**; when the thermolysis is carried out in an aprotonic medium like toluene, the corresponding 2-(tetrazol-5-yl)-4*H*-3,1-benzoxazin-4-one results [56]. The



51 52

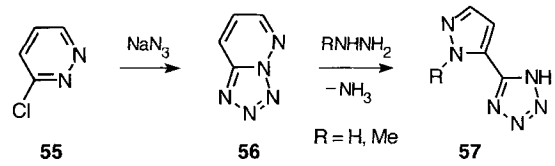
same type of conversion is reported for the pyridazine **53**. As with the spiro intermediate derived from **51**, C–C bond cleavage occurs between the sp^3 and the ketonic (not the amidic) carbon atoms. Heating **53** in dioxan or acetic acid containing water gives rise to the corresponding benzaldehyde hydrazone (**54**: H in place of CO_2Bu) [56].



53 54

Pyridazines

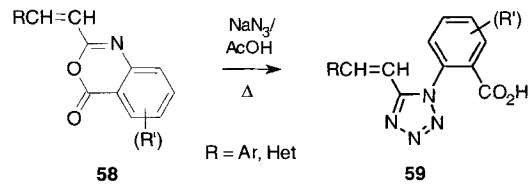
The tetrazolopyridazine **56**, made from **55**, reacts with hydrazines to give the pyrazolyl-substituted tetrazoles **57**. The driving force for this transformation is apparently the instability of the N(4)–N(5) bond in the non-aromatic intermediate (formed on addition of the nucleophile across the N(5)–C(6) bond): the related imidazo[1,2-*b*]pyridazine fails to react even under forcing conditions [57].



55 56 57

1,3-Oxaziniums, 4H-3,1-Benzoxazines (p. 193/vol. 2 in [1]; p. 24 in [2])

The scope of azidolysis of the mixed imidic-carboxylic anhydride functionality in 4*H*-3,1-benzoxazin-4-ones has been extended to substrates with unsaturated ligands at C(2), *e.g.* **58** which is a useful precursor to **59**. In addition, as with the related oxazol-5(4*H*)ones **18** the reagent hydrogen azide has been replaced with a mixture



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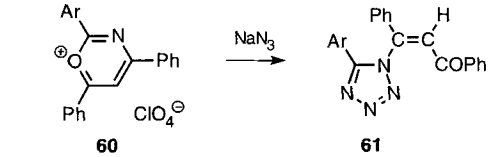
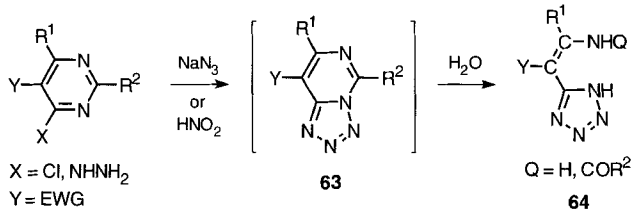


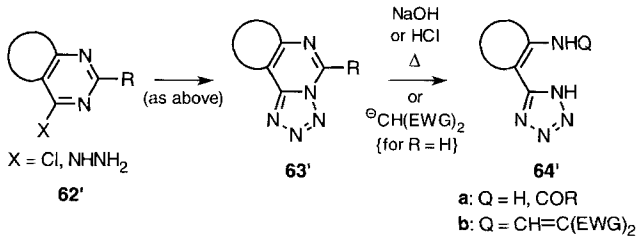
60 61

of sodium azide and acetic acid; in all cases 1-acylbenzimidazol-2(3*H*)-ones are formed as side products [58, 59]. Azide ion has been found to selectively attack C(2) of the cation in **60**, thereby producing the tetrazolyl-substituted chalcones **61** in high yield; the side chain in these compounds is (*Z*)-configurated [60].

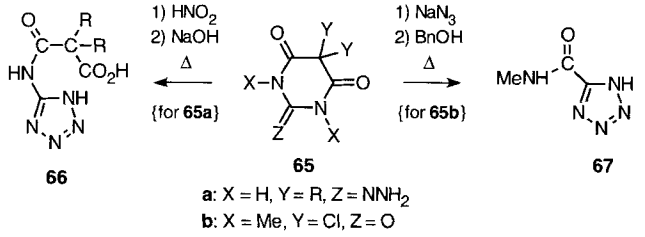
Pyrimidines (p. 97 in [2]), *Quinazolines, Purines*

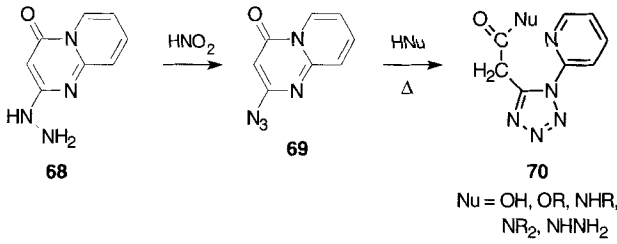
The highest number of examples for transforming a six-membered ring into a tetrazole derivative are found in the pyrimidine series. When compound **62** having EWG = NO_2 [61] or CO_2Et [62] are treated with sodium azide and nitrous acid, respectively, instead of the expected bicycles **63** the monocyclic tetrazoles **64** are obtained. The reaction proceeds under mild conditions, the driving force being the proclivity of **63** for covalent hydration of the C(5)–N(6) double bond whereupon isomerization to **64** occurs. In certain cases the COR^2 group is lost by hydrolysis [61c–e] or is found attached to N(1) of the tetrazole ring [61b]. Quite remarkably, also a pyrimidine which lacks the acceptor group at C(5) is capable of undergoing this transformation (**62**: X = $NHNH_2$; R^1 = Me, Cl; R^2 = H; H in place of EWG) [63a], but with the congener having $R^1 = NR_2$ the reaction stops at the bicyclic stage [63b].





Extension of this sequence to fused pyrimidine derivatives **63'** such as quinazolines [64] and purines [65] is possible, but here aqueous acid or a base is required to open the pyrimidine ring, frequently at elevated temperature. An interesting variant consists in the reaction of quinazoline and different pyridopyrimidines with carbanions (EWG = CO_2R, CN *etc.*) to give compounds of type **64'b** [66]. Likewise by a two-step procedure the pyrimidine derivatives **65** can be converted into the tetrazoles **66** [67] and **67** [56], respectively; for the crucial step to **67** which is formed in 42% yield, see also

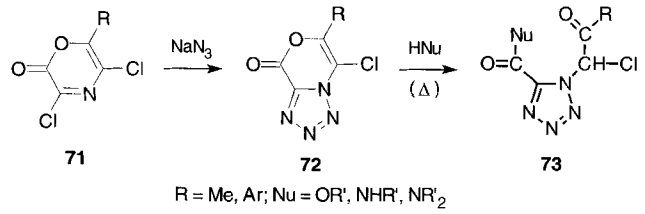




the behaviour of the diazides **51** and **53**. Finally, treatment of the pyridopyrimidine **69** (obtained from **68** almost quantitatively) with a range of protonic nucleophiles causes cleavage of the amide grouping whereupon the imidoyl azide formed cyclizes to the tetrazole **70** [68].

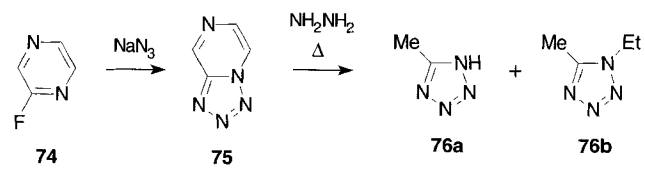
2H-1,4-Oxazines, 2H-1,4-Benzoxazines

Chloro-2*H*-1,4-oxazin-2-ones such as **71** are easily transformed into the fused derivatives **72** whose lactone functionality can be opened with nucleophiles like water, alcohols and amines to give the tetrazoles **73**. This sequence also proceeds well with the appropriate benzoxazinones [69].



Pyrazines

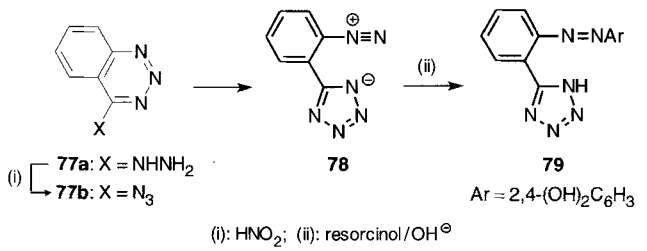
Low yields of the tetrazoles **76** result when the bicycle **75**, obtained from the pyrazine **74** [70], is submitted to prolonged heating in hydrazine hydrate. The formation of **76a,b** can be explained by an initial attack of the nucleophile at C(5) and C(8), respectively [71].



2.5 Six-membered rings with three or more heteroatoms

1,2,3-Benzotriazines

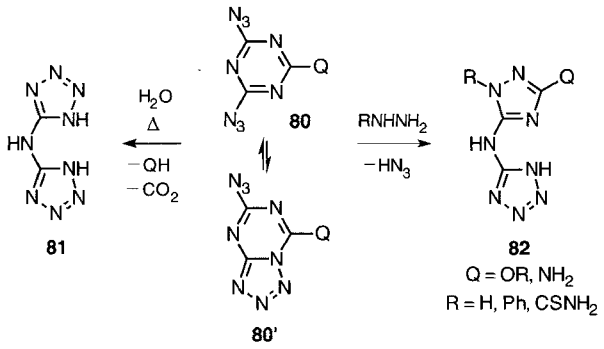
When the hydrazine **77a** is treated with sodium nitrite in acetic acid and then added to an alkaline solution of resorcinol, the tetrazole **79** is obtained – a result pointing to **78** as the intermediate [72a]. This material can be isolated as a crystalline solid when isoamyl nitrite is used as reagent but was thought to be the azide **77b** [72a]. Later work which clarified the structure also showed that **78** equilibrates with **77b** in methanolic solution [72b].



(i): HNO_2; (ii): resorcinol/$OH^{\ominus}$

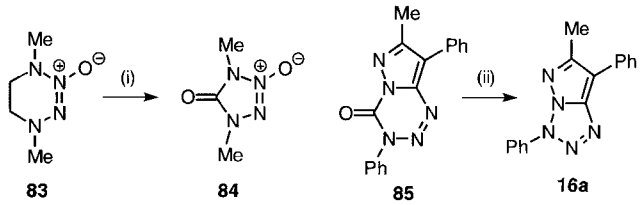
1,3,5-Triazines

The same kind of ring opening as encountered in the pyrimidine series (see above this Section) occurs with the azide **80** upon action of nucleophiles like water and hydrazines. The reaction passes through the isomeric tetrazolotriazine **80'** which undergoes addition of the nucleophile across the C(5)–N(6) double bond. With the reagent water, C(5) is then lost by hydrolysis to give **81**, while with hydrazines this carbon atom is built into the 1,2,4-triazole ring to afford **82** (*cf.* Section 3.4 on 1*H*-1,2,4-triazoles) [73].



1,2,3,4-Tetrazines, 1,2,3,5-Tetrazines

Ring contractions of tetrazines are rare. When the 1,2,3,4-tetrazine derivative **83** is treated with potassium permanganate at 70 °C, small amounts of the tetrazole **84** are obtained; by contrast, manganese dioxide yields a tetrazinone, and hydrogen peroxide cleaves the nitrogen chain [74]. With the fused 1,2,3,5-tetrazinone derivative **85** the carbonyl group can be split out by alkaline hydrolysis, and the resultant triazene of type **15** is then cyclized oxidatively to the new bicycle **16a** (*cf.* Section 2.2 on pyrazoles) [75].



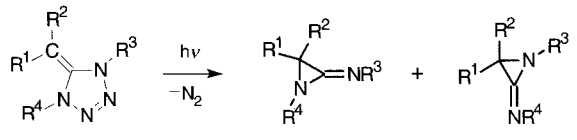
(i): $KMnO_4/\Delta$; (ii): NaOH, then $Pb(OAc)_4$

3 Tetrazoles converted into other rings

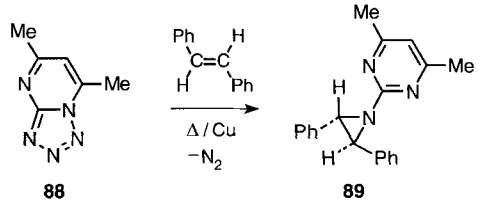
3.1 Three- and four-membered rings

Aziridines

Photolysis of 5-alkylidenedihydrotetrazoles like **86** quantitatively yields the aziridinimines **87** (diastereoselectively the (*E*)-isomers; with (*E*)/(*Z*) equilibration at room temperature) [76a,b]. These compounds are likewise formed on heating **86** at 100 °C, but their thermal instability causes [1+2] cycloreversion into isocyanide and imine [77] – a process that is also induced by UV irradiation below 300 nm [76b]. Bicyclic congeners of **86** are capable of undergoing this ring contraction, too [76c]. The copper-catalyzed decomposition of the fused tetrazole **88** in the presence of *trans*-stilbene affords 40% of the aziridine **89** (besides 3% of *cis* isomer) [78]. Another aziridine formation by nitrene to olefin cycloaddition is observed as side reaction on the thermolysis of *N*-(5-phenyltetrazol-2-yl)phthalimide in boiling cyclohexene [79].

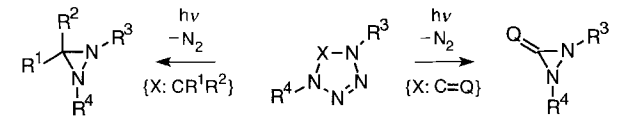


R^1, R^3 = Alk; R^2 = H, Alk; R^4 = Alk, Ar



Diaziridines

Submission of the dihydrotetrazoles **90** (X = CR^1R^2) to photolysis gives rise to diaziridines **91** in reasonable to good yield [80, 81], except when C(5) bears two unsaturated substituents [81]. Compounds **91** result also on thermolysis, but for application of this variant C(5) must be free of an aromatic ligand like phenyl since the latter causes [3+2] cycloreversion into azide and imine [81].



91 **90** **92**

R^1 = H, Alk, Ar
R^2 = H, Alk
R^3 = Alk, Ar; R^4 = Alk

Q = O, NAlk
R^3 = Alk, Alkenyl
R^4 = Alk

Diaziridines of type **92** are obtained on photolysis of the corresponding tetrazoles **90** [76a, 82]; a tris(imino)-methane species as the assumed precursor to **92** (Q = NAlk) has been detected by ESR spectroscopy at −195 °C [83a]. Limitations of the method exist with phenyl [84a,b] and alk-1-enyl ligands [84a] at the ring or exocyclic nitrogen atoms; in these cases benzimidazole derivatives are formed. Yet, irradiation of **90** (X = CO, R^3 = vinyl, R^4 = *t*-Bu) in argon or nitrogen matrices at 12 K yields the respective diaziridinone **92** [83b]. Attempts to generate diaziridinethiones (**92**: Q = S) by this route failed, all conditions led to carbodiimides [76a, 82, 83b]. These compounds are also formed on photolysis of **90** (X = C=NAlk), but they are mere side products [76a, 83b].

Direct formation of an alkylidenediaziridine **92** (Q = CMe_2, R^3 = $MeSO_2$, R^4 = Ar) occurs on treatment of a ketenimine with mesyl azide at room temperature [85]. Perhaps the reaction goes through the respective tetrazole **90** (*cf.* [86]).

1,3-Diazetidines

Small amounts of 1,3-diazetidinediimines were detected in the pyrolysate of certain 1-aryl-5-methyltetrazoles. These compounds are believed to arise from polymerization of the primarily formed carbodiimides followed by thermal degradation of the polymers [87].

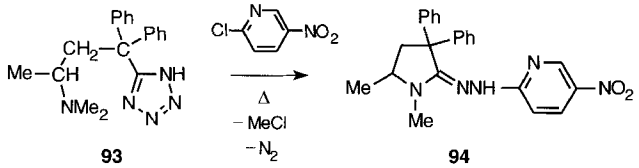
3.2 Five-membered rings with one heteroatom

Isobenzofurans

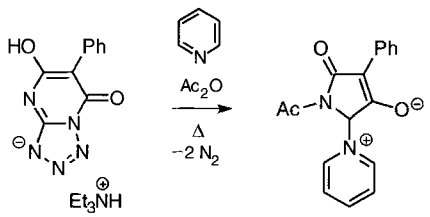
When *o*-(1-phenyltetrazol-5-yl)benzoic acid is strongly heated, the reaction described in Section 2.2 proceeds reverse [88]. However, under the severe conditions the *N*-phenylphthalisoimide initially formed rearranges to the phthalimide isomer which is obtained virtually quantitatively as cited below.

Pyrrolidines, Indoles, Isoindoles (p. 92 in [2])

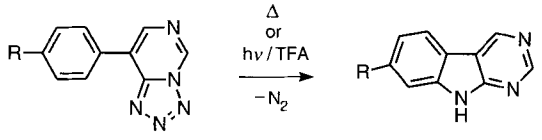
An unusual transformation occurs on treating the tetrazole **93** with 2-chloro-5-nitropyridine in boiling pyridine. The process passes through a nitrile imine whose carbon atom is intramolecularly attacked by the amine function to give, after loss of methyl chloride, the semicyclic amidrazone **94** [89]. Likewise unique appears the formation of the pyrrole derivative **96** from the fused tetrazole **95**; the actual pathway leading to the product (which results in high yield) is not yet settled [90]. Photocyclization of the fused system **97** in TFA affords excellent yields of the indole derivatives **98**. Photolysis or thermolysis in nonpolar solvents, however, slows down the process and gives poorer yields [91]. Remarkably, a substrate having the pyrimidine ring in **97** replaced with a pyrazine unit virtually fails to react in this manner because here ring contraction of the intermediary azinylnitrene is favoured over C–H insertion [92]. Finally, a 3*H*-indole is formed along with other components on thermolysis of the spiro compound **160** (R^1, R^2 = Me; R^3, R^4 = Ph; see Section 3.4 on 1*H*-1,2,3-triazoles); the product arises *via* ring expansion of a transient aziridine **87a** or **b** [77b].



93 **94**



95 **96**



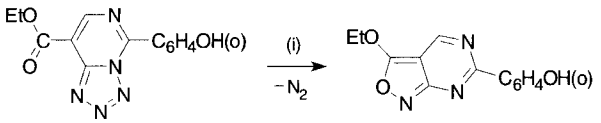
97 **98**

R = H, Me, MeO, Cl

3.3 Five-membered rings with two heteroatoms

Isoxazoles

The tetrazolopyrimidine **99** which predominantly exists as the azide affords the fused isoxazole **100** when it is thermolyzed in either the solid state or dissolved in dry DMSO [62b]. The conversion can also be achieved photolytically. In this case **100** is accompanied by the product formed through stabilization of the triplet nitrene, *i.e.*, the corresponding azo compound [93]. Attempts to bring about an analogous transformation with a 4-benzoyltetrazoloquinoline failed [94]. Cyclization of 2-nitrobenzonitrile imines to 2,1-benzisoxazole *N*-oxides is not observed if the dipole bears an acyl or azin-2-yl substituent at the nitrogen atom [95] (*cf.* Section 3.4 on 4*H*-1,2,4-triazoles and 1,3,4-oxadiazoles).

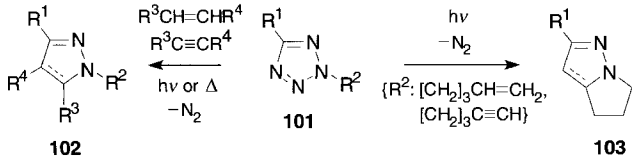


99 **100**

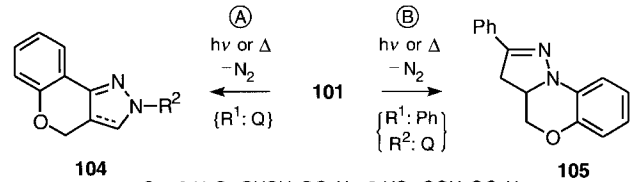
(i): Δ / dry DMSO or Δ / neat or hν/C_6D_6

Pyrazoles (pp. 405, 406 in [1]; pp. 88, 90 in [2]), *Indazoles*

Thermolysis or photolysis of 2*H*-tetrazoles **101** generates nitrile imines which can be trapped by alkenes (also cyclic ones) and alkynes to give, respectively, dihydropyrazoles and pyrazoles **102** with a wide variety of substituents (for examples other than those reviewed in [1, 2] and [96], see [79, 97–101]). Accordingly, tetrazoles **101** bearing suitably shaped alkenyl or alkynyl residues undergo an intramolecular cycloaddition to the fused systems **103** [102], **104** [102a, 103] and **105** [103c]. The process **101** → **103** which has been studied in great detail fails with substrates having for R^2 an allyl or but-3-enyl group, but on addition of DMAD the formation

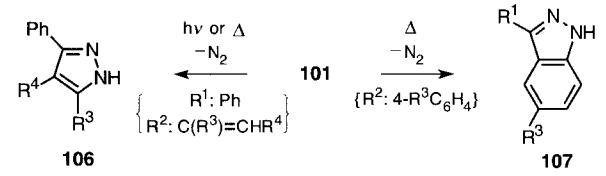


102 **101** **103**



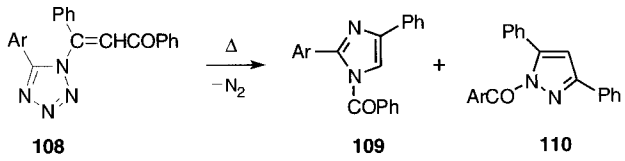
104 **105**

Q = 2-H_2C=$CHCH_2OC_6H_4$, 2-HC≡$CCH_2OC_6H_4$

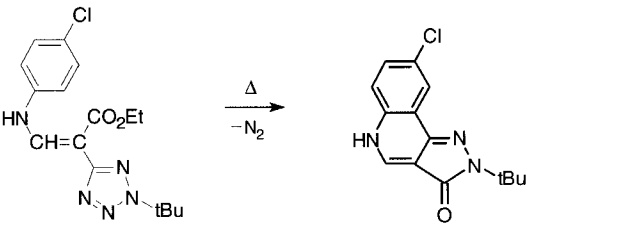


106 **107**

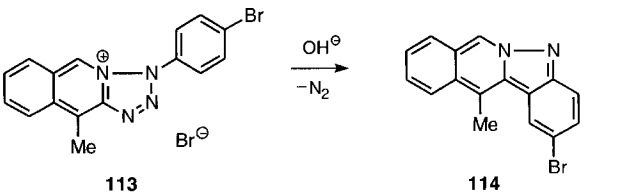
of type **102** is not hampered [102a]. Reaction "A" can be extended to **101** where Q = 2-(but-3-enyloxy)phenyl to give the respective benzoxepinopyrazole [103c]. Nitrile imines generated from **101** that have an alk-1-enyl ligand at nitrogen undergo electrocyclization to yield, after a 1,3-*H* shift, the pyrazoles **106** (in part quantitatively) [104, 105]. Substrates with R^2 = C(Ph)=C($SnBu_3$)CO_2Et [105] as well as C($POPh_2$)=C(NMe_2)$_2$ [106] do not give stable 4*H*-pyrazoles because the $SnBu_3$ and NMe_2 ligands migrate too. The phenylogous parallel to this interconversion – the formation of indazoles **107** – has been realized by submitting **101** (R^1, R^2 = Ar) to FVP or heating in boiling tetraline [107a]. Isomers of **107**, *i.e.*, 6-substituted 1-phenylindazoles, have been detected by MS in the thermolysate of **101** (R^1 = 4-RC_6H_4, R^2 = Ph) [107b].



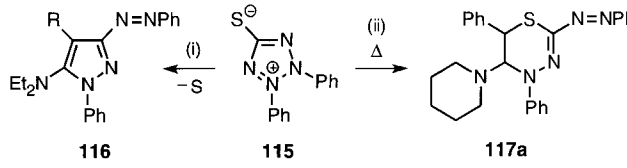
108 **109** **110**



111 **112**



113 **114**



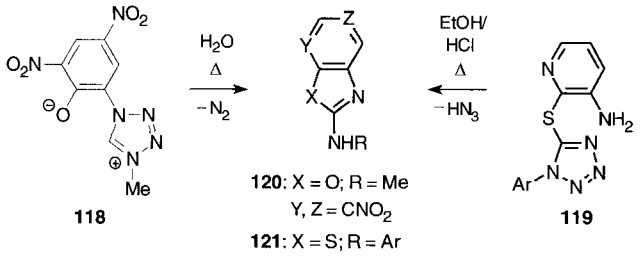
116 **115** **117a**

(i): Et_2NC≡CR; (ii): $[CH_2]_5$NCH=CHPh

An unexpected course is observed on thermolysis of the tetrazoles **108** performed in an inert solvent: besides the regular product **109** (see this Section on imidazoles) the pyrazole **110** is formed in 30% yield; the reaction is thought to go through a 1-(β-benzoyl-α-phenylvinyl)diazirine which isomerizes to a 1,3,4-oxadiazepine as the immediate precursor to **110** [108]. A result that resembles the formation of **94** (see Section 3.2 on pyrrolidines *etc.*) constitutes the conversion of **111** into the fused system **112** (15% yield); the desired tetrazolyl-substituted quinolin-4(1*H*)-one was not obtained from this experiment [109]. Treatment of the tetrazoloisoquinolinium salt **113** with tetramethylammonium hydroxide at room temperature gives rise to the fused pyrazole **114** (in addition to 40% of the respective benzaldehyde formed through ring opening of the pyridine unit in **113**) [52b]. Finally, when the open-chain valence isomer of dehydrodithizone (**115**) – 1,5-diphenylthiocarbodiazone – cycloadds to ynamines, the products (*i.e.* 4*H*-1,3,4-thiadiazines) extrude sulfur to afford pyrazoles like **116** in good yield; for R = Me also traces of the regioisomers are found [110a,c]. Cycloaddition to enamines gives 5,6-dihydro-4*H*-1,3,4-thiadiazines like **117a** which, by contrast, are stable [110c]. Simply heating **115** in boiling acetic acid leads to the benzothiadiazine derivative **117b** (see this Section on thiazoles *etc.*) [111].

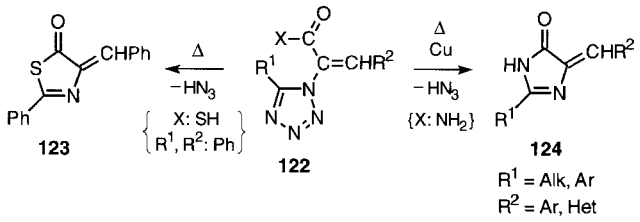
Oxazoles, Benzoxazoles

Attempts to decarboxylate the α-(tetrazol-1-yl)acrylic acids **19** have shown that the reaction **18** → **19** (see Section 2.2 on oxazoles) is reversible at high temperatures as demonstrated in detail for **19** having R^1, R^2 = Ph and R^3 = H [25]. Upon warming an aqueous solution of **118** at 60 °C the 2-aminobenzoxazole **120** is obtained in moderate yield; 1,4-disubstituted tetrazolium ions are known to give carbodiimides – the actual intermediate – under mild conditions [112].

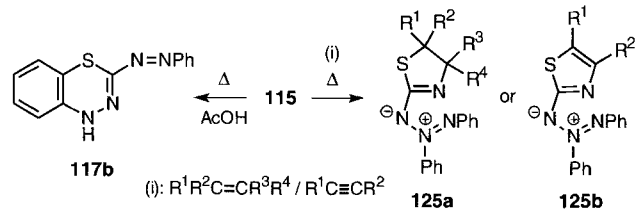


Thiazoles, Benzothiazoles

In analogy to the aforementioned process **19** → **18**, thermolysis of the thiocarboxylic acid **122** (X = SH) leads to the thiazolone **123** (see also this Section on imidazoles) [113]. When 3-amino-2-(tetrazol-5-ylthio)-pyridines such as **119** are heated in an acidic medium,

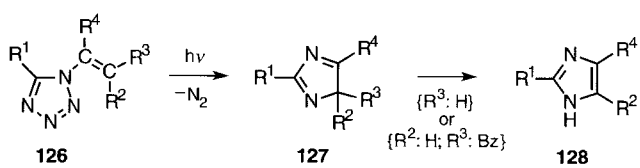


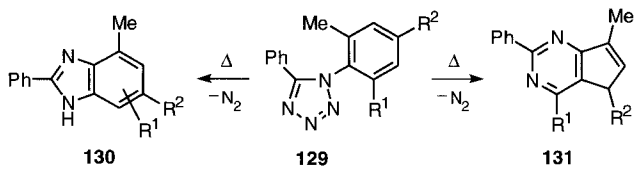
these compounds, instead of undergoing a Smiles rearrangement, are transformed into the fused system **121** (the intended rearrangement, however, takes place if the tetrazole substituent at N(1) is alkyl or aralkyl) [114]. In contrast to enamines and ynamines (see this Section on pyrazoles *etc.*), electron-depleted alkenes and alkynes including benzyne cycloadd to dehydrodithizone (**115**) in a [2+3] fashion, thereby producing thiazole derivatives like **125** [110c, 115]. These compounds were originally thought to be thiazolo[3,2-*d*]tetrazoles, until X-ray studies disclosed their open-chain structure [115b,c]. The different behaviour of **115** towards electron-rich and electron-poor systems has been rationalized through FMO theory [110c].



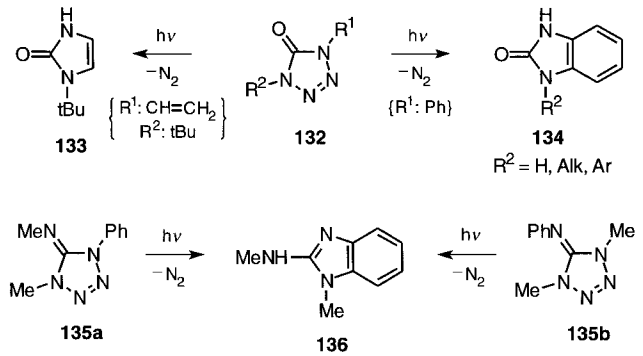
Imidazoles, Benzimidazoles (pp. 403, 410, 411 in [1]; pp. 91, 92 in [2])

Copper-catalyzed thermolysis of the acrylamides **122** (X = NH_2) affords the imidazolones **124** (10–60% yield) [113]. Side products are imidazoles of type **128** (R^4 = $CONH_2$) which arise preferably when **122** (X = NH_2) is thermolyzed *in vacuo* [116]. The principle of this latter conversion has been developed into an efficient route to both 1*H*- (**128**) [105, 117] and 4*H*-imidazoles (**127**) [118] by photolyzing vinyltetrazoles **126** with a wide variety of substituents. If the double bond in the side chain of **126** belongs to a phenyl or 2-furyl group, thermolysis or even mass spectral fragmentation gives rise to benzimidazoles [10, 87, 119] or a furo[2,3-*d*]imidazole [120]. This transformation also works with substrates such as **129** (R^1 = Me), although here carbodiimides

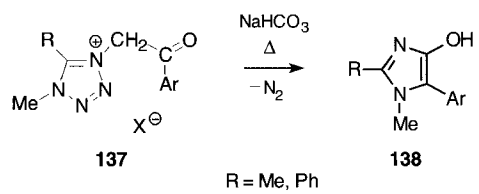


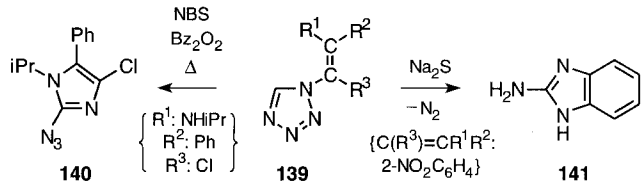


are major products [121a]. Common intermediate on the pathway to **130** and **131** is a 3a*H*-benzimidazole; if both *ortho* substituents in **129** are methoxy, the group becoming attached to C(3a) is split off as formaldehyde. Photolysis of **129** having $R^1 = CO_2R$ and $R^2 = H$, however, proceeds with migration of the ester group to the benzimidazole nitrogen atom [121b]. An acyl shift to imidazole nitrogen (giving compound **109**; see this Section on pyrazoles) also occurs on aromatization of the putative 4*H*-derivative **127** (R^1 = Ar, R^2 = COPh, R^3 = H, R^4 = Ph) [108]. Photolysis of the appropriate vinyltetrazolone **132** performed in solution (see, however, Section 3.1 on diaziridines) affords the imidazolone **133** in high yield [84a]. If **132** is phenyl-substituted, the benzimidazolones **134** are obtained, even with an alk-1-enyl group present at the opposite nitrogen atom [84c]. As expected, the aminobenzimidazole **136** is formed on photolysis of **135a**; this product also arises from the isomer **135b**, and a mixture of two benzimidazoles is found if one methyl group is replaced with phenyl – results that point to the intermediacy of a tris(imino)methane diradical [84d].

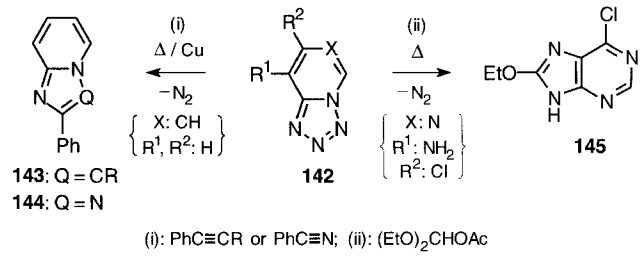


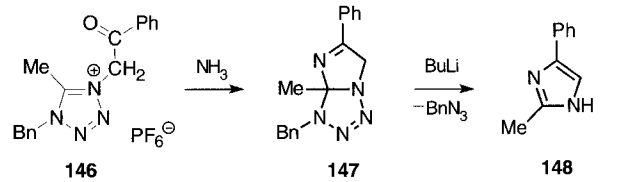
Treatment of the salts **137** with a weak inorganic base at 80–100 °C affords low to moderate yields of the imidazoles **138**; the reactive species is the corresponding ylide which (in the case R = Me) fails to give a pyrrolotetrazole as the properly expected product [122].

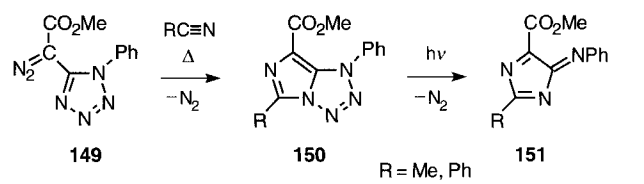




The imidazole **140** is obtained in >60% yield when the enamine function of the respective substrate **139** is oxidatively linked to the tetrazole carbon; the resultant bicycle spontaneously ring-opens [69b]. The benzimidazole **141** has been isolated in an attempt to reduce the nitro group of 1-(2-nitrophenyl)tetrazole (**139**: R^1–R^3 as shown) with sodium sulfide; the reaction obviously goes through a cyanamide which is a known degradation product of base-exposed 1-aryltetrazoles [123]. Small quantities of **143** result on copper-catalyzed thermolysis of tetrazolopyridine (**142**: X = CH, R^1, R^2 = H) in the presence of alkynes [78]. Converting the amino group of the tetrazolopyrimidine **142** (X = N, $R^1 = NH_2$, R^2 = H) into an imidate function at elevated temperature leads directly to the fused imidazole **145** [124]. The dihydroazapentalene **147**, obtained from the phenacyltetrazolium salt **146**, loses benzyl azide on deprotonation to give the imidazole **148** in 20% yield [125]. UV irradiation of the cycloadduct **150** which is easily obtained from the (diazoalkyl)tetrazole **149** constitutes an interesting route to the less common class of 4*H*-imidazol-4-imines (**151**) [28b].



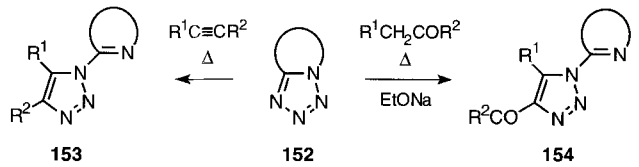


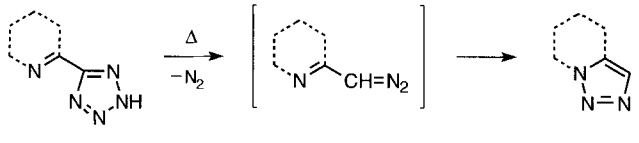


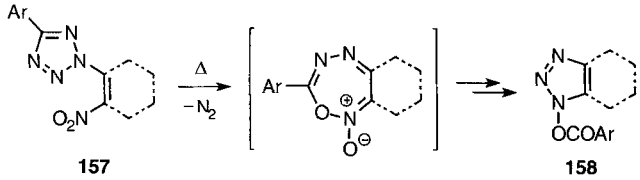
3.4 Five-membered rings with three or more heteroatoms

1H-1,2,3-Triazoles (p. 78 in [2])

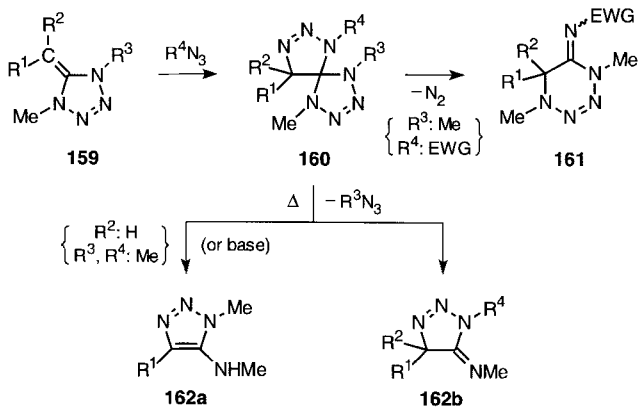
Derivatives **152** in which the non-tetrazolic half-ring represents a (substituted) pyridine [126], pyrimidine [126a], pyridazine or pyrazine unit [127] are converted to 1-azinyl-1,2,3-triazoles **153** when heated in the presence of alkynes (preferably acceptor-substituted ones). The extension to olefins is limited [126a]. Substrates **152** having a ring-fused benzothiazole or 1,2,4-triazine moiety react with 1,3-dicarbonyl compounds to give the triazoles **154** or their 1-defunctionalized congeners [128]. 5-Azinyltetrazoles **155** (azinyl = 2-pyridyl, pyrazin-2-yl, quinazolin-4-yl), thermolyzed in the gas phase or in solution, are a source for fused triazoles like **156**; their direct precursor is a diazo compound which arises by a 1,3-*H* shift of the primarily generated nitrile imine [129]. Pyrolysis of 2*H*-tetrazoles **157** that have a 2,4-dinitrophenyl [130] or a substituted 5-nitropyrimidin-4-yl ligand [95] at N(2) gives high yields of the triazole derivatives **158**; ring contraction of the 1,2,5,6-oxatriazepine unit is followed by an N→O acyl shift. For the behaviour of the 1*H*-isomer of **157**, see this Section on 2*H*-1,2,3-triazoles.





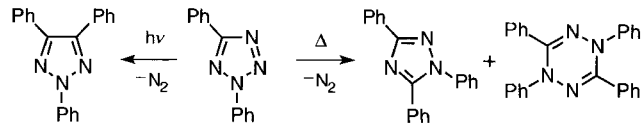


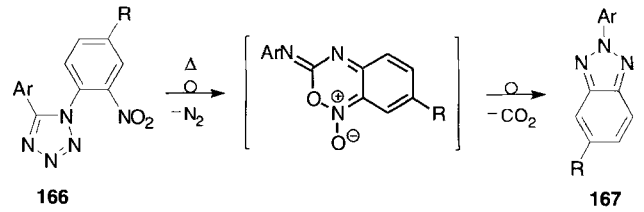
5-Alkylidenedihydrotetrazoles **159** readily add alkyl azides to give the spiro derivatives **160**. The tetrazole ring in these species is opened thermally [77, 131b] or, if R^2 = H, also by base [131a] to yield the triazoles **162a** and **b**, respectively. Since thermolysis (or even moisture) liberates azide likewise from **159**, the triazoles **162** can arise directly [77a]; from **159** (R^1, R^2 = H; R^3 = Me) the corresponding triazole is formed at room temperature [131c]!

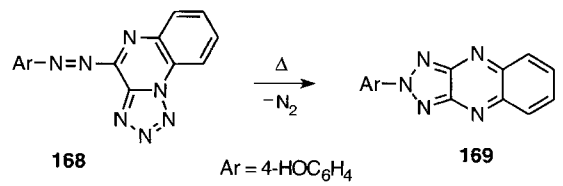


2H-1,2,3-Triazoles (p. 403 in [1])

Head-to-head photodimerization of diphenyl nitrile imine, generated from 2,5-diphenyltetrazole (**101a**), leads to the triazole **163** as a side or major product [98b, 132a–c]; traces of this compound may also be detected in trapping experiments with the dipole molecule [132d]. Remarkably, formation of the analogous 2-methyltriazole by photolysis of 2-methyl-5-phenyltetrazole does not go through a nitrile imine [133]. Thermolysis of 5-aryl-1-(*o*-nitrophenyl)tetrazoles such as **166** gives high yields of 2-arylbenzotriazoles **167**; the reaction proceeds *via* a carbodiimide which is attacked by the nitro group. Starting tetrazoles with an inverse substitution pattern afford only poor yields of **167** under the same conditions; the reason is enhanced thermal stability of the



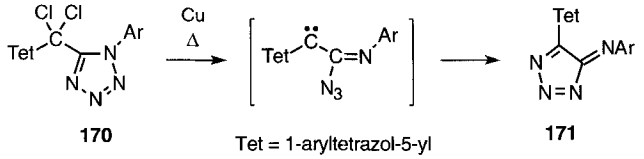




tetrazole as well as slower migration of the *o*-nitrophenyl group after the ring has opened [134]. Finally, as the result of a nitrene–diazene interaction the fused triazole **169** is obtained in over 70% yield on heating compound **168** in boiling DMF [135].

4H-1,2,3-Triazoles

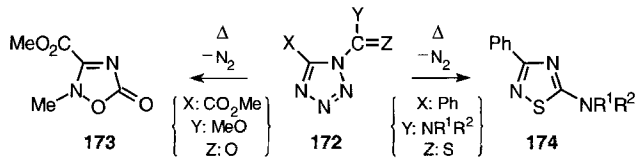
Thermolysis of the dichlorobis(tetrazolyl)methane **170** in the presence of copper powder affords the unique 4*H*-triazole derivative **171** in fair yield [136].



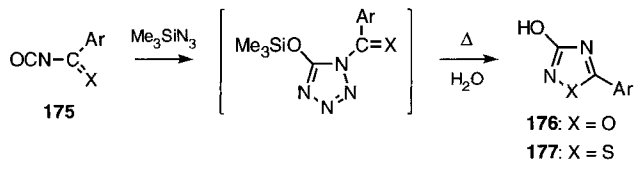
170 **171**

1,2,4-Oxadiazoles (p. 412 in [1])

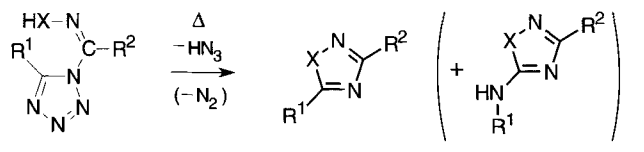
Instead of giving the methyl ester of 5-methoxy-1,2,4-oxadiazole-3-carboxylic acid (as observed upon photolysis [1]), the tetrazole **172** (X = CO_2Me, Y = MeO, Z = O) on being heated in tetraline at 185 °C yields the isomeric oxadiazolone **173** [137]. 3-Hydroxy-1,2,4-oxadiazoles **176** (and likewise their thio analogues **177**) result directly in excellent yield when (thio)aroyl isocyanates **175** are treated with trimethylsilyl azide at elevated temperature [138]. A patent claim of making 3-aryloxy/arylthio-1,2,4-oxadiazoles through acylation of *N*-unsubstituted tetrazoles and ensuing thermolysis [139a] is at variance with [139b]. Pyrolysis of 1-hydroximoyltetrazoles **178** (X = O), obtained from addition of the *N*-unsubstituted tetrazoles to nitrile oxides, affords oxadiazoles such as **179** [140]. If C(5) of **178** (X = O) is unsubstituted, the amino derivatives **180** (R^1 = H) are found as side products – an outcome of the competing carbodiimide (cyanamide) formation from **178** (X = O) [140b] (for the related process **178** (X = NAr) → **181/182**, see this Section on 1*H*-1,2,4-triazoles).



173 **172** **174**



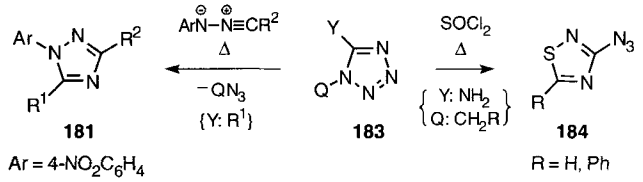
175 **176**: X = O **177**: X = S



178 **179**: X = O **181**: X = NAr **180**: X = O **182**: X = NAr

1,2,4-Thiadiazoles

Heating 1-(thiocarbamoyl)tetrazoles (**172**: X, Y, Z as shown) in boiling chlorobenzene gives high yields of the aminothiadiazoles **174** [141]. The same principle underlies the formation of the hydroxythiadiazoles **177** [138]. A rather unusual transformation is observed when 5-aminotetrazoles (**183**: Y = NH_2, Q = CH_2R) are treated with excess thionyl chloride at elevated temperature; the reaction which gives **184** in moderate yield apparently proceeds through stepwise sulfinylation of the *C*- and *N*-substituents [142], it fails when Q = Et [142b].

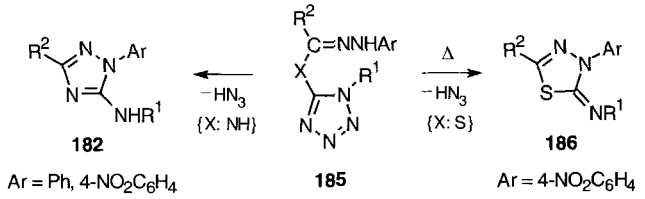


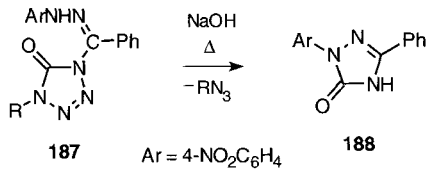
181 **183** **184**

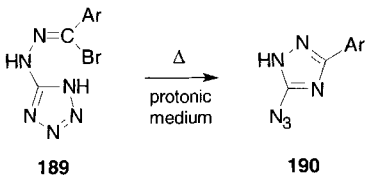
1H-1,2,4-Triazoles (pp. 403, 407, 409 in [1]; pp. 68, 84, 86–88, 90 in [2])

Copper-catalyzed thermolysis of tetrazolopyridine (**142**: X = CH, R^1, R^2 = H) in the presence of benzonitrile gives rise to the fused triazole **144** in fair yield; this reaction mode is also observed with alkynes (see Section 3.3 on imidazoles) [78]. Thermal degradation of 2,5-diphenyltetrazole (**101a**) leads to the triazole **164** and the di-hydrotetrazine **165** as main products (see this Section on 2*H*-1,2,3-triazoles) [107b, 143a]; the same applies to the 5-(4-cyanophenyl) analogue [143b]. This contrasts with photolysis upon which 1,2,4-triazole formation is negligible [98b, 132b,d, 133]. In close parallel to the behaviour of **178** (X = O) (see this Section on 1,2,4-oxadiazoles), 1-hydrazonoyltetrazoles **178** (X = NAr; R^1 = Alk, Ar) on being heated at >100 °C (partly in an acidic medium) afford the triazoles **181** [140b, 144] and/or – depending on substituents – the derivatives **182** [140b]. Particularly prone to giving **181** are the substrates **178** (X = NAr) with R^1 = H or Cl, R^2 = Ph, Ar = 4-$NO_2C_6H_4$ [144], and also with R^1 = NH_2 or NHAlk the conversion proceeds under milder conditions [144, 145], while in the case of R^1 = 2,6-$Cl_2C_6H_3$ no reaction occurs [144b]. Interestingly, the triazole type **181** can also arise from cycloaddition of a nitrile imine across the N(4)–C(5) bond of certain 1*H*-tetrazoles **183**; the intermediary dihydro-triazolotetrazole stabilizes by [3+2]

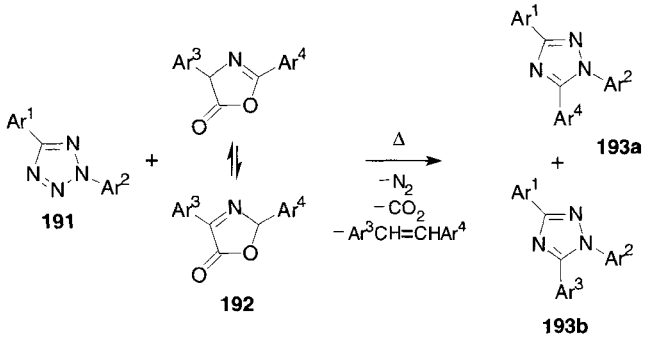
cycloreversion into azide and the target triazole (not unlike the process **147** → **148**; see Section 3.3 on imidazoles). The ease of this conversion is enhanced by electron-releasing groups at C(5)-linked aryl substituents; no reaction takes place with the 2*H*-isomers of **183** [146]. Direct formation of **182** is observed when 1-substituted 5-aminotetrazoles are treated with hydrazonoyl halides, the primary products **185** (X = NH) elude isolation [144b, 145]. The thio analogues (**185**: X = S), however, require heat for the conversion into **186**, and to bring about the transformation **187** → **188** alkali is needed in addition [147]. Finally, treating hydrazonoyl bromides like **189** with aqueous organic solvents causes intramolecular imidoylation followed by spontaneous opening of the tetrazolic half-ring to give the triazole derivative **190** [148]. The process can in part be compared to the formation of the azido-imidazoles **140** (see Section 3.3 on imidazoles).

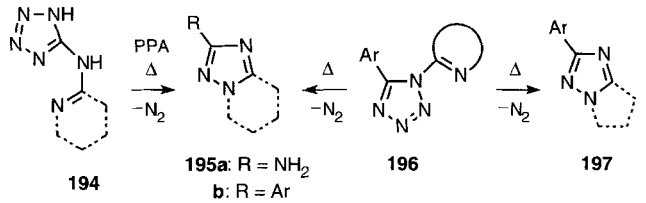






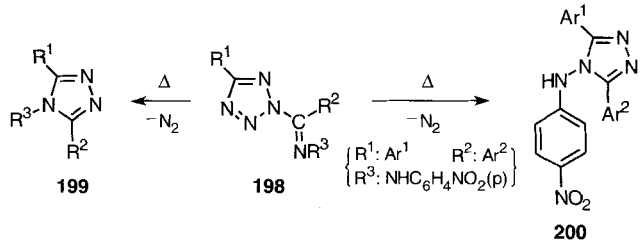
Nitrile imines, thermally generated from the tetrazoles **191**, add to the C=N double bond of the isomerizing 5(4*H*)-oxazolones **192**. Subsequent extrusion of carbon dioxide from the resultant bicycle and loss of the ylidic side chain as stilbene leads to a mixture of the triazoles **193** [149]. The overall reaction thus equals the well-known [3+2] cycloaddition of nitrile imines to nitriles; for examples (beyond those surveyed in [1, 2]), see [150]. Fused triazoles **195a** are obtained in moderate to fair yield when tetrazoles **194** having a (2-pyridyl)-, (pyrimidin-2-yl)- or a (pyrazin-2-yl)amino group are heated in polyphosphoric acid [151]. By a similar nitrene reaction, performed in inert solvents, the bicyclic derivatives **195b** arise from 5-aryltetrazoles **196** that have a 2-pyridyl [152a] or a pyrimidin-2-yl moiety [152b] attached to N(1). Accordingly, azapentalenes **197** result when **196** bears a thiazol-2-yl [153b,e], a 1,3,4-thiadiazol-2-yl [153c,e], a benzo- or dihydronaphthothiazol-2-yl [153a,f] or a benzimidazol-2-yl group [153d].



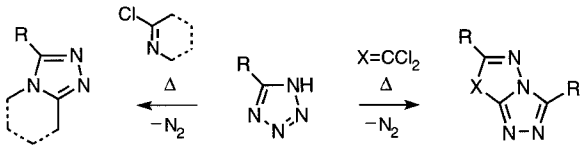


4H-1,2,4-Triazoles (pp. 400, 403 in [1]; pp. 81, 87, 88 in [2])

2-Imidoyltetrazoles **198**, most frequently treated *in situ*, are easily converted into triazoles **199** upon heating (for examples other than those cited in [1, 2], see [154–156]). The more recent of these studies, however, show that **198** having R^3 = Ar exhibits dichotomous behaviour: depending on the nature of Ar and on conditions, the nitrile imines generated from **198** can cyclize to give either **199** or a 3*H*-1,3,4-benzotriazepine [155a, 156] (see Section 3.7). Thermolysis of 2-hydroximoyltetrazoles **198** (R^3 = OH) does not yield the expected 4-hydroxytriazoles **199** (R^3 = OH) [140, 157], and 2-hydrazonoyltetrazoles **198** (R^3 = NR) are said to give 1,2,4,5-tetrazines rather than 4-aminotriazoles [140b]. This however is at variance with [144b,c] where formation of the questionable class (**200**) is demonstrated. Another con-



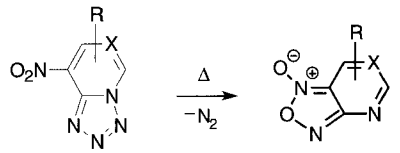
version into a 4-amino-1,2,4-triazole derivative is observed on thermolysis of 5-substituted 2-silyltetrazoles [150a]. Fused-ring analogues of **199** – *i.e.*, compounds of type **202** – result on heating 2-(azin-2-yl)tetrazoles which are made from **201** and most often thermolyzed *in situ*; for material beyond that mentioned in [1, 2], see references [89, 95, 158, 159] which describe derivatives having a pyridine, pyridazine, pyrimidine or pyrazine substructure. Employment of bifunctional reagents like isocyanide dichloride or thiophosgene consequently leads to the azapentalenes **203** [160] and **204** [161]; the formation can be viewed as proceeding *via* a 2-(azol-2-yl)tetrazole (for the thermolysis of such species, see [162]).



202 **201** **203**: X = NR **204**: X = S

1,2,5-Oxadiazoles (p. 411 in [1]; p. 92 in [2])

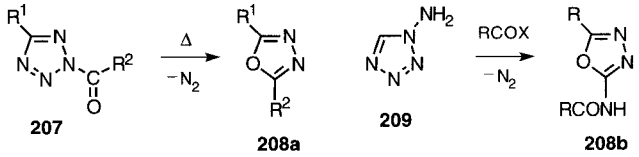
For the long-known transformation of 8-nitrotetrazolopyridine (**205**: X = CH, R = H) into the respective furazan derivative **206**, improved preparative procedures have been developed [163]. Substrates having electron-withdrawing groups (**205**: X = CNO_2, R = H) [50] and/or an additional ring nitrogen (**205**: X = N) [61a,c] show enhanced reactivity. An extension of this scheme to oxo- and dioxo-substituted 8-nitrotetrazolo[1,5-*c*]pyrimidines is possible [61a,b].



205 X = CH, N **206**

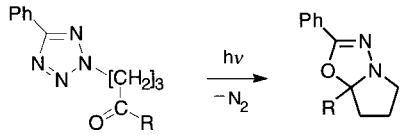
1,3,4-Oxadiazoles (pp. 394, 396, 397, 409 in [1]; pp. 79–81, 85 in [2])

The well established process **207** → **208a** (the oxalogue of the conversion **198** → **199**) is of prime importance for the synthesis of unsymmetrically substituted 1,3,4-oxadiazoles. The reaction is broadest in scope, it has recently been reviewed [164] and also studied theoretically [165]; for cases in addition to those surveyed in [1, 2, 164], see [89, 95, 159d, 166–168]; a rare limitation of the method became recently apparent in the failure to prepare a derivative **208a** with R^2 = (tetrazol-2-yl)methyl [169]. Interestingly, attempts to acylate the



207 **208a** **209** **208b**

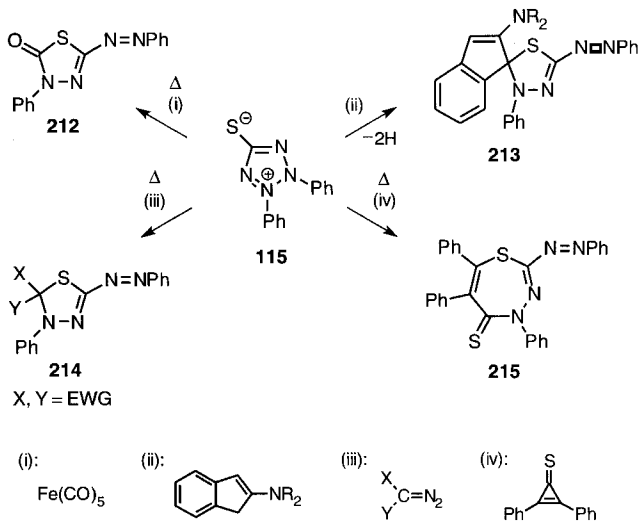
amino group of **209** under mild conditions led directly to **208b** [170]; the reaction most probably goes through a 1,4-disubstituted tetrazolium ion with subsequent formation of a carbodiimide (*cf.* the process **118** → **120**; Section 3.3 on imidazoles). The long-known conversion of 2*H*-tetrazoles into dihydro-1,3,4-oxadiazoles by degradation in the presence of an aldehyde or ketone [1, 2] has found an intramolecular parallel (**210** → **211**) [171].



210 **211**

1,3,4-Thiadiazoles (pp. 400, 401, 409, 410 in [1]; p. 80 in [2]), *1,2,3,4-Thiatriazoles* (p. 412 in [1])

In addition to work already mentioned in this Section on 1*H*- and 4*H*-1,2,4-triazoles [**185** (X = S) → **186** and **201** → **204**, respectively], attention is drawn to conversions of dehydrodithizone (**115**). As in the case **115** → **116/117a** (see Section 3.3 on pyrazoles), this compound reacts as open-chain valence isomer (the thiocarbodiazone) to give the thiadiazolone **212** by heating with pentacarbonyliron [172] and the spiro compounds **213** upon exposure to 2-(dialkylamino)indenes [110b,c]. The derivatives **214** result on heating with acceptor-substituted diazoalkanes or on treatment of the bromine adduct of **115** with the carbanions of the respective

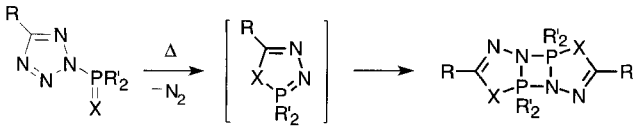


212 **115** **213** **214** X, Y = EWG **215**

methylene compounds [173]. In acidic solution **214** reverts to **115** having S–CHXY in place of S^- [174]. – Apparently no new example for the transformation of a tetrazole into a 1,2,3,4-thiatriazole is available.

1,3,4,2λ⁵-Thia(selena)diazaphospholes

2-Thiophosphoryltetrazoles **216** (X = S), made by thiophosphorylation of the respective *N*-unsubstituted tetrazoles, readily lose nitrogen to yield the transformation products **217** (X = S), the monomers remaining inobservable [175a]. The precursors **216** (X = S) result also on successive employment of chlorophosphines and sulfur; this variant is used for preparing the selenium analogues **217** (X = Se) [175b].

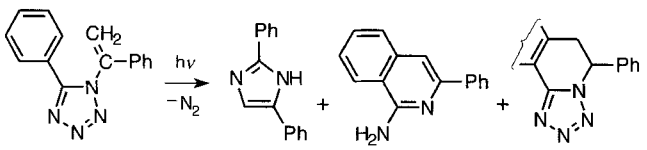


216 X = S, Se **217**

3.5 Six-membered rings with one or two heteroatoms

Isoquinolines

Photolysis of the vinyltetrazole **218** yields the expected imidazole **128a** in moderate yield; however, as major side product arises the aminoisoquinoline **219** (formed besides traces of **220** which was ruled out to be the precursor) [117b].



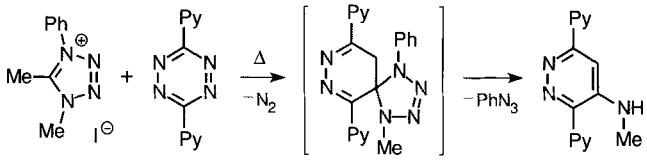
218 **128a** **219** **220**

Pyridazines

Heating the tetrazolium salt **221** with the 1,2,4,5-tetrazine shown and triethylamine in ethanolic solution produces the (methylamino)pyridazine **222** in high yield [176]; the intermediary spiro compound – the outcome of a Diels–Alder reaction with inverse electron demand – behaves like **160** when giving **162a** or **b** (see Section 3.4 on 1*H*-1,2,3-triazoles).

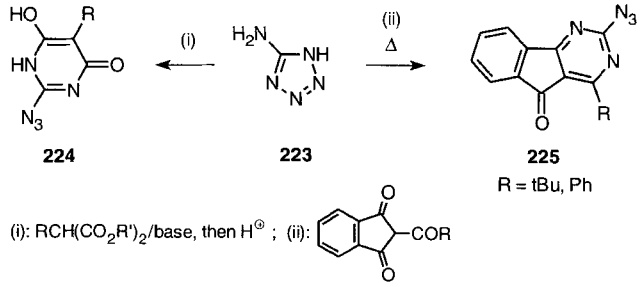
Pyrimidines (p. 411 in [1]; pp. 92, 99 in [2]), *4H-3,1-Benzoxazines* (p. 92 in [2])

Quite a number of transformations dealt with here result from an inherent lability of acceptor-substituted tetra-



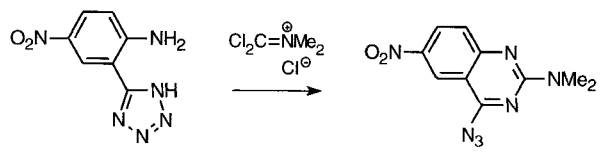
221 Py = 2-pyridyl **222**

zolo[1,5-*a*]pyrimidines with respect to their open-chain valence bond isomers (the 2-azidopyrimidines). Thus, cyclization of 5-aminotetrazole (**223**) with the bifunctional reagents shown directly gives the derivatives **224** [90, 177a] and **225** [178] (exclusively or besides the bicyclic isomers); the same holds for the reaction of **223** with substituted malonaldehyde [179]. Similarly, treatment of the phenylogue **226** with Viehe's salt affords the azidoquinazoline **227** [180]. 2-Amino-5,6,7,8-tetrahydroquinazoline is obtained unexpectedly on treating **223** with ethyl (2-oxocyclohexyl)glyoxylate [181]. In other cases isolable cyclization products like **228** and **230a,b**

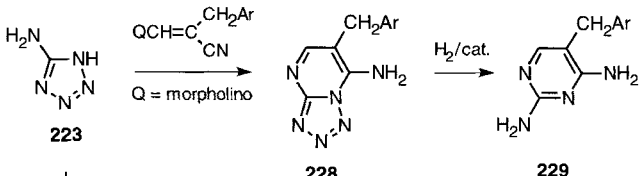


224 **223** **225** R = tBu, Ph

(i): $RCH(CO_2R')_2$/base, then $H^{\oplus}$; (ii):

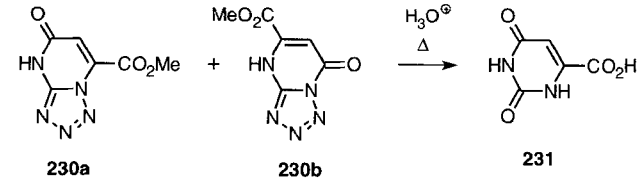


226 **227**



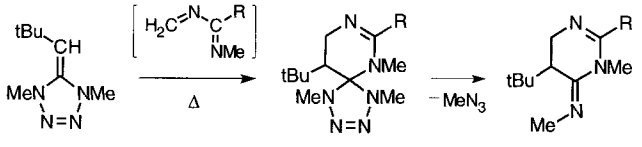
223 **228** **229**

DMAD



230a **230b** **231**

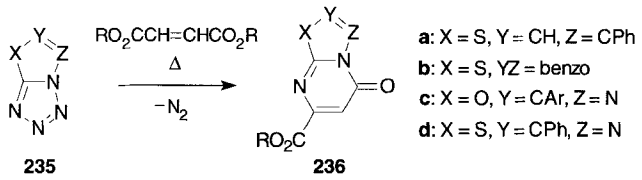
are converted into the pyrimidines **229** [182] and **231** [177b] when submitted to hydrogenolysis and hydrolysis, respectively. A unique transformation is observed on thermolysis of the alkylidenedihydrotetrazole **232**. This species cycloadds to the diazadiene fragment (produced from part of **232**) to give the spiro compound **233** which in turn loses methyl azide to yield the pyrimidine **234** (*cf.* the formation of **162a,b**; Section 3.4 on 1*H*-1,2,3-triazoles) [77a].



232 **233** **234**

R = CH_2tBu

The old conversion of tetrazolopyridine into a pyridopyrimidine by heating with a fumarate [1, 2] has found several imitations which include the processes **235a,b** → **236a,b** [183], **235c** → **236c** [183a, 184] and **235d** → **236d** [185]. Benzimidazole- and 1,2,4-triazine-fused pyrimidinones are available too [183a], but here also in the solid state the precursors exist as azides (regarding **235c**, data is conflicting [183a, 184]). For the formation of a cyclopentapyrimidine, see the behaviour of tetrazole **129** (Section 3.3 on imidazoles). – Apparently no new report has appeared on 4*H*-3,1-benzoxazines.

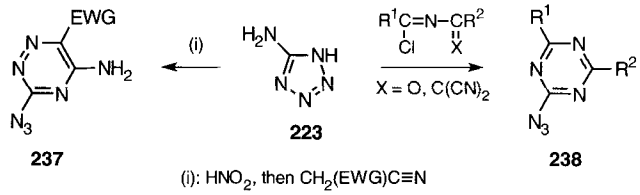


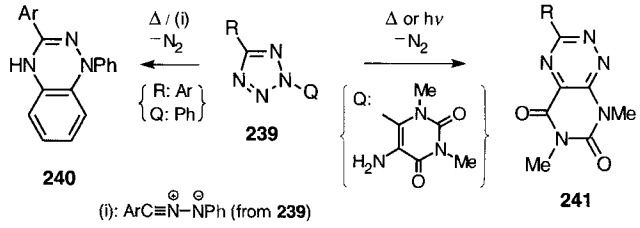
235 **236**

3.6 Six-membered rings with three or more heteroatoms

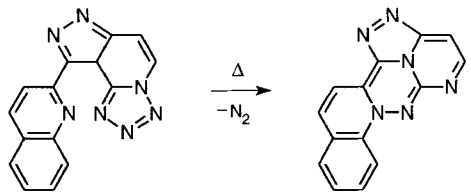
1,2,4-Triazines, 1,2,4-Benzotriazines

Annulation of 5-aminotetrazole (**223**) by successive diazotization and coupling to malono- or nitroacetonitrile gives rise to the open-chain valence isomers **237** (*cf.* **223** → **224**; this Section on pyrimidines) [186]. As regards extension of the principle shown in **122** → **123/124** (see Section 3.3 on imidazoles) to an α-(tetrazol-1-yl)cinnamohydrazide (**122**: X = $NHNH_2$; R^1, R^2 = Ph), this experiment resulted in loss of the functional group rather than in cyclization to a 1,2,4-triazine [113]. As an additional component the 1,2,4-benzotriazine **240** has been detected by computer-aided MS analysis of a thermolyzed 5-aryl-2-phenyltetrazole (**239**: R and Q as shown); the initially formed nitrile imine cycloadds in a





[3+3] manner to phenylnitrene [143b]. Intramolecular cyclization of the nitrile imine derived from the uracil-substituted tetrazoles **239** leads to the fervenulins **241** in high yield [187]. Finally, formation of an azacyclazine bearing a 1,2,4-triazine unit (**243**) occurs straightforwardly on thermolysis of the fused tetrazole **242** [188].



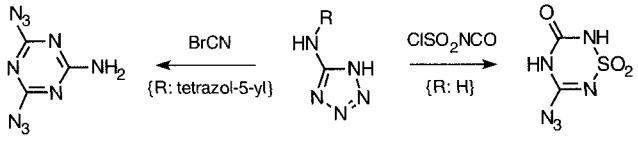
242 **243**

4H-1,3,4-Thiadiazines, 4H-1,3,4-Benzothiadiazines

These systems can arise from dehydrodithizone (**115**) as already shown in connection with the pyrazole- and thiazole-forming transformations (see **115** → **116/117a, b**; Section 3.3) [110a,c, 111].

1,3,5-Triazines (p. 87 in [2])

Formation of this ring by trimerization of cyanamide or carbodiimide fragments is observed on thermal decomposition of the parent tetrazole [189], of its 5-amino derivative (**223**) [190] and of 1-substituted 5-iodotetrazoles [191]. Transformations that result from instability of the respective tetrazolotriazines are effected on treatment of **223** with *N*-acylimidoyl chlorides (or equivalents) which affords azidotriazines **238** in 30–80% yield [192]. Likewise, formal linking of the two rings in bis(tetrazol-5-yl)amine (**244**) with cyanogen bromide gives the triazine derivative **245** (65% yield) [193].



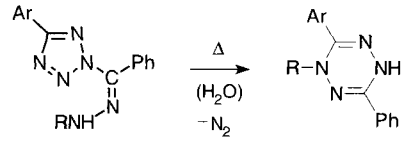
245 244 246

1,2,3,4-Tetrazines

A remarkable transformation of methylenedihydrotetrazoles **159** takes place when these compounds are treated with electrophilic azides such as sulfonyl, phosphoryl, picryl and 2,4-dinitrophenyl representatives (see Section 3.4 on 1*H*-1,2,3-triazoles). In this case the initially formed spiro derivatives **160** (which are not isolable), instead of giving triazoles **162a** or **b**, extrude molecular nitrogen and, *via* a rare 1,2-*N* shift, afford the tetrahydrotetrazinimines **161** in high yield [194]; cleavage of **160** into dihydrotetrazolimine and a diazo compound may occur to a small extent [194a]. Derivatives **160** where R^4 = 2- or 4-$NO_2C_6H_4$ are stable at room temperature, but mild thermolysis also gives **161** [77b].

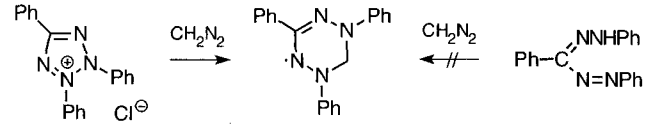
1,2,4,5-Tetrazines (pp. 403, 404 in [1]; pp. 86–88 in [2])

Symmetrically substituted 1,4-dihydro-1,2,4,5-tetrazine derivatives are obtained on thermolysis of 2,5-diaryltetrazoles [107b, 143a] (see Section 3.4 on 1*H*-1,2,4-triazoles). 3,6-Diphenyl-1,2,4,5-tetrazine appears in trace amounts when *N*-(5-phenyltetrazol-2-yl)toluenesulfonamide is heated in an aqueous medium [195]. Tetrazine formation on photolysis is observed in particular with *N*-unsubstituted 5-phenyltetrazole [98a, 132a, 196]. Thermolysis of 2-hydrazonoyltetrazoles like **247**, performed in a protonic medium, preferably gives the tetrazines **248** (>70% yield) instead of the isomeric 4-aminotriazoles **200** (*cf.* Section 3.4 on 4*H*-1,2,4-triazoles) [144c]. The tetrazine structure has also been assigned to the transformation products obtained in a previous study from several 2-hydrazonoyltetrazoles (among them examples having aliphatic substituents such as ethyl in place of Ar



247 248

R = 4-$NO_2C_6H_4$



249 250 251

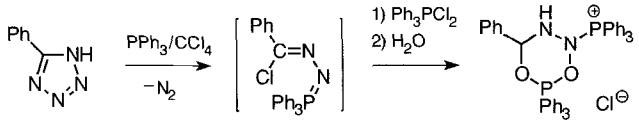
and phenyl) [140b]. A rather exceptional tetrazine formation constitutes the conversion of **249** into the verdazyl **250** on treatment with diazomethane; the reaction was shown not to go through the formazan **251** [197].

2H-1,2,4,6-Thiatriazines

The thiatriazine derivative **246** is formed in high yield upon reaction of 5-aminotetrazole (**244**: R = H) with chlorosulfonyl isocyanate; because of easy hydrolysis to (tetrazol-5-yl)urea, **246** is an attractive precursor to this compound [198].

1,3,4,5,2λ⁵-Dioxadiazaphosphinanes

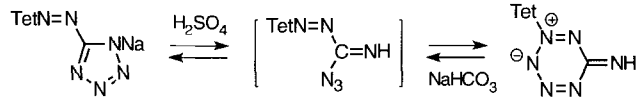
When 5-phenyltetrazole (**252**) is subjected to the Appel reaction, a complex sequence leads to a 2-[(phosphoranediyl)hydrazonoyl]tetrazole and a salt-type substance that has been assigned structure **253** [199].



252 253

Pentazines

Brief treatment (5–7 sec) of an excess of the disodium salt **254** with dilute mineral acid gives about 40% of the mesoionic pentazine **255** (a previously unknown class); acid in excess, however, destroys the six-membered ring, leading to 5-[(diazomethyl)azo]tetrazole (**254**: CH=N_2 in place of Tet; H in place of Na). Compound **255** (of which also some ^{15}N analogues were made) is so unstable as to lose nitrogen when dissolved in water or organic solvents (*e.g.* DMF, DMSO) even with cooling [200].



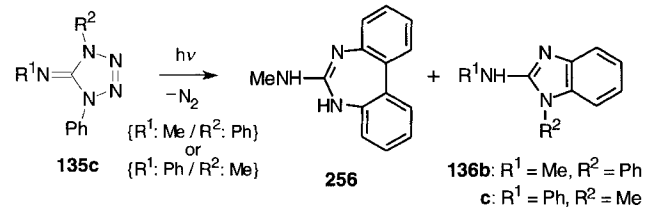
254 255

Tet = tetrazol-5-yl (sodium salt)

3.7 Seven-membered rings

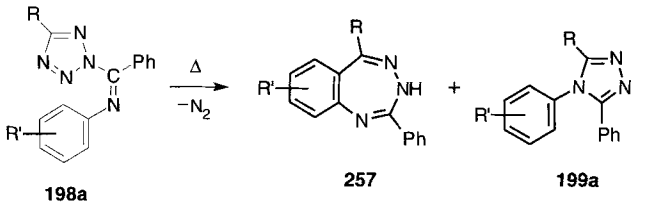
1H-1,3-Diazepines

Photolysis of the dihydrotetrazolimine **135c** (each isomer) generates, in addition to the pair of benzimidazoles **136b,c**, the fused 1,3-diazepine **256** [84d] (*cf.* Section 3.3 on imidazoles).



3H-1,3,4-Benzotriazepines

As pointed out in Section 3.4 (4*H*-1,2,4-triazoles), thermolysis of 2-imidoyltetrazoles like **198a** can produce high yields of the benzotriazepines **257** (either alone or accompanied by the triazoles **199a**) [155, 156]. The reaction is considered a major preparative route to this class of compounds [201].



1,3,4-Thiadiazepines

Dehydrodithizone (**115**) reacts with diphenylcyclopropenethione in boiling benzene to give the thiadiazepine **215** in moderate yield (see Section 3.4 on 1,3,4-thiadiazoles); again, the open-chain valence isomer of **115** – the thiocarbodiazone – is involved [115d].

4 Concluding Remarks

The foregoing pages demonstrate that tetrazoles – subject to suitable type, reagents, conditions and substituents – are sources for a wide variety of heterocycles. It is also shown that, *vice versa*, a considerable number of tetrazoles result from other ring systems, quite often very readily. In either section processes stand out that have an important synthetic potential; particularly weighty among them appear interconversions that allow the synthesis of functionalized derivatives less easily accessible by conventional methods. However, besides those preparatively useful transformations (which deserve further "exploitation") there are numerous conversions that attract primarily because of their (partly unknown) mechanisms.

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