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N-Heterocycles *via* oxidative intramolecular cyclization

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This review highlights two principal strategies of the last years (since 2015) for the design of various N-heterocycles including those containing O, S, Si, Se, Te heteroatoms *via* oxidative intramolecular cyclization using different catalysts, oxidants and reaction conditions.
The bibliography includes 132 references.

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1. Introduction

In the present review, the reactions of oxidative intramolecular cyclization are considered with a focus on the formation of *N*-heterocycles, mainly based on the literature over the last 3–5 years. The interest in these reactions stems from the versatility of the methods, pharmacological importance of the products, and the possibility of further transformations by introducing biologically active moieties. Two oxidative strategies are depicted schematically in Fig. 1. The first one implies the formation of the C–N bond by abstraction of two hydrogen atoms from the terminal CH and NH groups (*route 1a*) or from OH (SH) groups and azomethine CH groups (*route 1b*) induced by an external oxidant. The intramolecular version (*route 1c*) is also possible. The second strategy is a two-step process starting with the addition of an N-oxidized reagent or the *in situ* formed intermediate to the C=C bond and followed by cyclization *via* dehydrohalogenation to aziridines or oxazolines (*routes 2a*, *2b*) or, in the case of solvent interception, to imidazolines, oxazolines (*route 2c*) or 1,4-oxazocanes. Some of these reactions were reviewed covering the literature up to 2018,[1,2] so, the present review focuses on progress in this field in recent years.

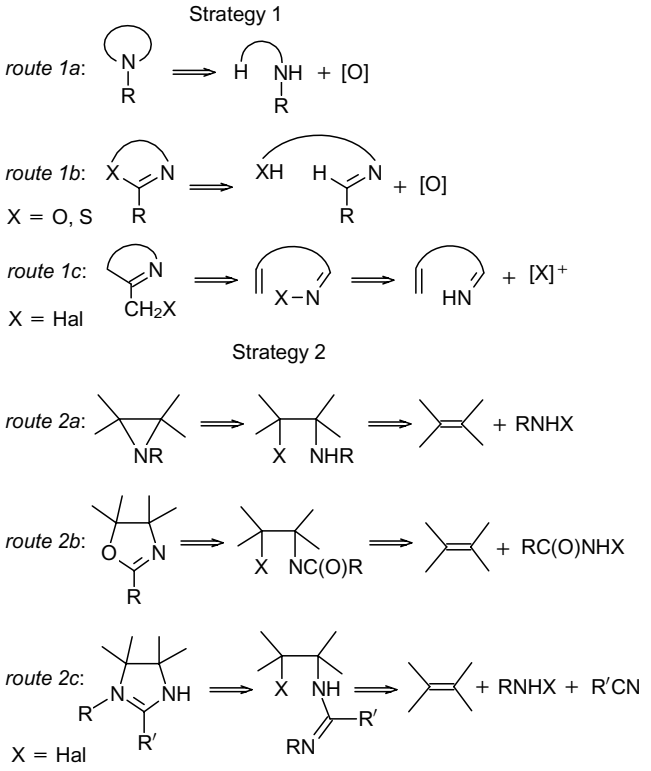


Figure 1. Retrosynthetic routes to different N-heterocycles.

The review is not limited to specific methods or a class of heterocycles; for this, the reader is encouraged to refer to relevant reviews, such as a recent review on hypervalent iodine-induced cyclizations,[3,4] syntheses of various heterocycles *via* aerobic oxidation,[5] the Ir-catalyzed oxidative cyclization of alkenyl amides,[6] or a comprehensive 2022 review[7] on the synthesis of imidazo[1,2-*a*]pyridines including intramolecular oxidative heterocyclization reactions.

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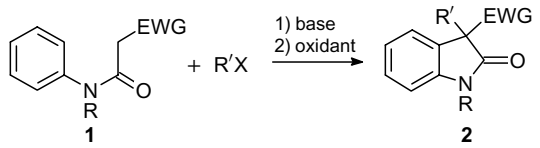
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2. Intramolecular heterocyclization *via* dehydrogenative C–C, C–X or N–X bond coupling

2.1. C–C bond coupling

The literature of 2008–2017 on the metal-catalyzed oxidative amination of different C–H bonds leading to 5-membered *N*-heterocycles is partly summarized in a review,[8] which includes also hydroamination and intermolecular cycloaddition reactions. The analysis below highlights the studies over the last decade of intramolecular dehydrogenative heterocyclizations involving various X–H bonds. This is an effective strategy for the synthesis of various *N*-heterocycles, which can be performed either by the action of an external oxidant or using a pre-oxidized reagent. Thus, metal-catalyzed or metal-free dehydrogenative cyclization with the $C(sp^2)-C(sp^3)$ bond formation (Scheme 1) was shown to lead to the 2-oxindole structural motif present in many natural alkaloids[9] (see also references cited therein).

Scheme 1

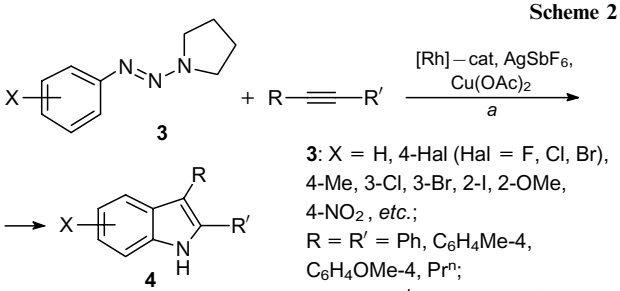


EWG = COOMe, CN; oxidant is I_2, NIS; NIS is *N*-iodosuccinimide

Indoles have also been prepared by oxidative cyclization of aryltriazenes **3** and **5** bearing an acetylenic moiety in the intermolecular[10] and intramolecular oxidative manner[11] (Scheme 2).

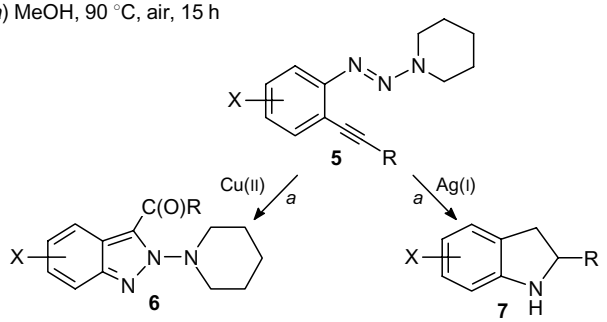
Iodine, as a mild and inexpensive oxidant, was used for intramolecular dehydrogenation of *N*-(3-arylbut-3-en-1-yl)anilines **8** with the C–C bond formation to give

Scheme 2



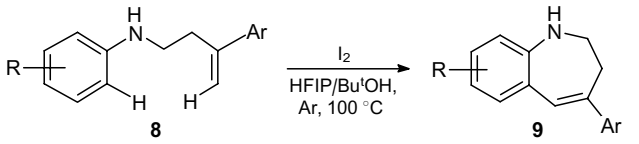
3: X = H, 4-Hal (Hal = F, Cl, Br), 4-Me, 3-Cl, 3-Br, 2-I, 2-OMe, 4-NO_2, *etc.*;
R = R′ = Ph, C_6H_4Me-4, C_6H_4OMe-4, Pr^n;
R = Me: R′ = Ph, cyclo-C_6H_{11}

(*a*) MeOH, 90 °C, air, 15 h



5: X = H, 4-F, 4-Cl, 2,4-Cl_2, 2-CO_2Me, 4-Cl; R = Ph, C_6H_4Y (Y = 4-F, 3-Me, 3-NH_2, *etc.*), cyclo-C_3H_5, cyclo-C_6H_{11}

Scheme 3

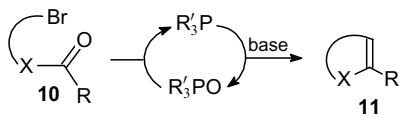


8: R = 4-Cl, 4-Me, 4-Et, Bu^t, Hal (Hal = F, Cl, Br), CF_3;
Ar = Ph, C_6H_4X-4 (X = F, Cl, Br, OMe, Bu^t, *etc.*);
HFIP = $(CF_3)_2CHOH$

benzo[*b*]azepines **9** in moderate to good yields (Scheme 3).[†, 12]

The intramolecular Wittig reaction of the carbonyl-containing bromides **10** including those having O, N, S heteroatoms was reported as an efficient method for the synthesis of isoquinolin-1(2*H*)-ones, indoles, 2,3-dihydro-1*H*-2-benzazepin-1-ones, benzofurans and 1,2-dihydroquinolines **11** *via* the C=C ring closure (Scheme 4). The main advantage is the use of a catalytic amount of phosphine oxide in the presence of $(Me_2SiH)_2O/Ti(OPr^i)_4$ as a reducing agent.[13]

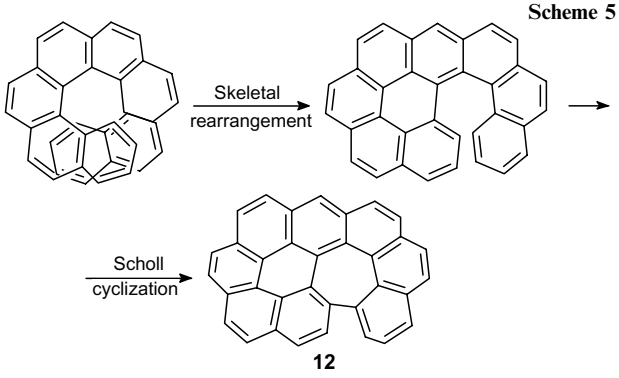
Scheme 4



X = C, O, NR_2, S

Finally, let us consider the recently reported oxidative cyclorearrangement of helicenes,[14] which, at first glance, is not related to the formation of N-heterocycles shown in Scheme 5 on the example of carbo[8]helicene, followed by the Scholl-type cyclization *via* dehydrogenation.[15] However, this reaction includes not only carbohelicene **12** but also helicenes with nitrogen or sulfur atoms on the periphery,[14] which justifies the inclusion of this work in the present review.

Scheme 5

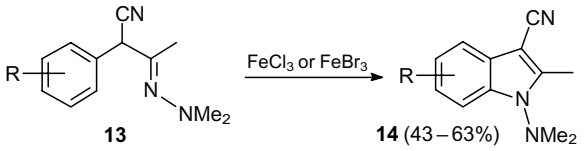


2.2. C–N bond coupling

Oxidative cyclization with formation of the C–N bond by the action of an external oxidant is the most common approach to *N*-heterocycles. One of such studies, referring

† Hereinafter, yields of ~100% are referred to as quantitative, >90% are excellent, >80% are very good, >70% are good, >50% are moderate, <40% are poor.

Scheme 6



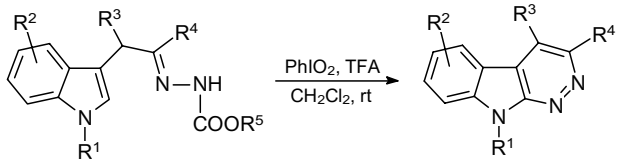
R = H, 2-Me, 3-OMe, $-OCH_2O-$, 3,4-$(OMe)_2$, *etc.*

to the beginning of the period under consideration, describes the synthesis of indole derivatives under the action of mild oxidant such as $FeCl_3$ or $FeBr_3$ on 3-(2,2-dimethylhydrazono)-2-arylbutanenitriles **13** to afford the target X-substituted 1-(dimethylamino)-2-methyl-1*H*-indole-3-carbonitriles **14** in moderate yields (Scheme 6).[16]

The proposed mechanism includes a single electron transfer (SET) from the α-position to the nitrile group with the reduction of FeX_3 to FeX_2, the elimination of HX molecule, and the second SET from the hydrazine nitrogen culminating in the indole ring closure. Close analogues of hydrazones **13**, containing OR group instead of NMe_2, under the action of $PhICl_2$ at room temperature give *N*-alkoxy-3-cyanoindoles in up to 98% yield.[17]

It has recently been shown that indoles **15** with a hydrazone motif in the 3-position undergo oxidative cyclization to azacarbolines **16** on treatment with iodoxybenzene $PhIO_2$ under mild conditions (Scheme 7).[18]

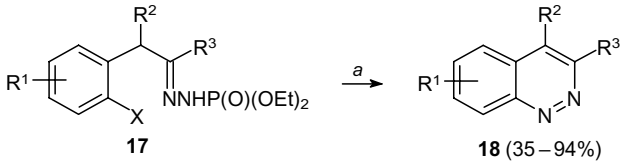
Scheme 7



R^1 = Me, Pr^n, Bn; R^2 = H, Me, OMe, OBn, *etc.*;
R^3 = CO_2Me, CO_2Et, $P(O)(OMe)_2$, *etc.*;
R^4 = Me, Pr^n, CH_2CO_2Et, *etc.* TFA is CF_3CO_2H; Bn = CH_2Ph

Copper acetate-induced annulation of phosphorylated hydrazones **17** accompanied by elimination of the X substituent to form the $C(sp^2)-N$ bond was proposed as a direct approach to cinnolines **18** (Scheme 8).[19]

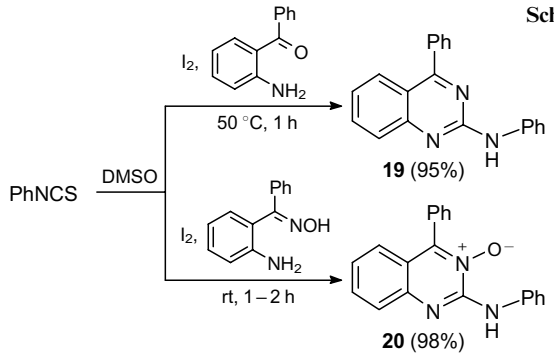
Scheme 8



(*a*) $Cu(OAc)_2$, toluene, air, 110 °C; X = H, F, OMe, or NMe_2;
R^1 = Bu^t, Br, CF_3, NO_2, *etc.*; R^2 = H; R^3 = Ph, Ar, Het;
R^2-R^3 = 5,6-naphthylidene

Substituted quinazolines **19**, which are isomeric to compounds **18**, and quinazoline *N*-oxides **20** were prepared by the reaction of phenyl isothiocyanate with benzophenone and its oxime by a metal-free protocol using molecular iodine (Scheme 9).[20]

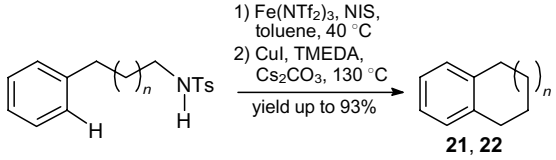
Scheme 9



5*H*-1,4-Benzodiazepines, quinazoline homologues, were obtained by a catalyst-free aerobic cyclization of aromatic amines and α-hydroxy ketones.[21]

One-pot, two-step intramolecular $C(sp^2)-N$ formation was described to afford indolines **21** and tetrahydroquinolines **22** *via* Fe(III)/Tf_2NH-catalyzed iodination, followed by Cu(I)-catalyzed intramolecular N-arylation (Scheme 10).[22]

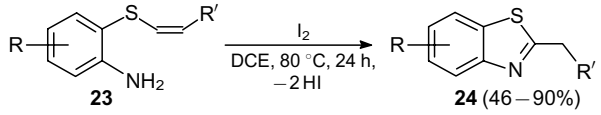
Scheme 10



n = 0 (**22**), 1 (**22**); Tf = CF_3SO_2

The cyclization of *ortho*-substituted anilines **23** initiated by molecular iodine as an oxidant was proposed as a route to 2-substituted benzothiazoles **24**[23] proceeding, as is evident from Scheme 11, as iodine-mediated elimination of NH and SCH hydrogen atoms; the yields range from moderate to good. Alternative approaches using oxidative, photochemical or metal-catalyzed cyclizations were compiled in a recent study.[24]

Scheme 11



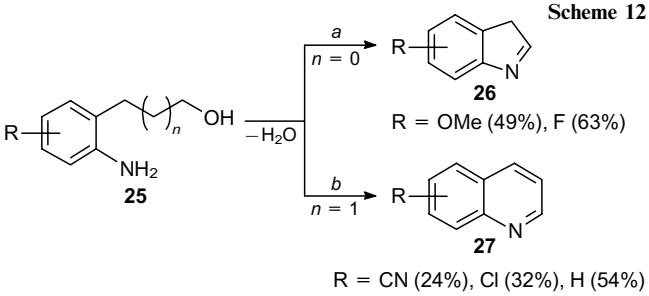
R = 3-Me, 4-Cl; R′ = Ar, CONHPh; DCE = $Cl(CH_2)_2Cl$

For the synthesis of substituted indoles or quinolines, the reaction of dehydration–oxidative cyclization of *ortho*-ω-hydroxyalkyl-substituted anilines **25** by heating in acetonitrile with TEMPO as an oxidant and $Cu(OTf)_2$ as a catalyst was employed (Scheme 12).[25] The yields ranged from moderate to good. Note that while the synthesis of indoles **26** was 'pure', the formation of quinolines **27** was complicated by the formation of up to 20% of 1,2,3,4-tetrahydroquinolin-2-ones as by-products.

Previously, it was demonstrated that *N*-tosyl-*o*-allylaniline in the presence of $CuBr_2$ undergoes Pd(II)-catalyzed bromoamination with cyclization to 5-(bromomethyl)-1-tosylpyrrolidin-2-one, although a considerable amount of dibromide was formed.[26]

In the pioneering work on metal-catalyzed enantioselective aminohalogenation of alkenes, Bovino and Chemler[27]

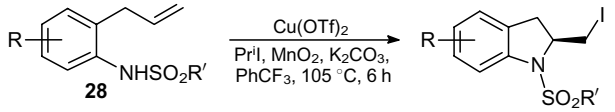
Scheme 12



(*a*) $Cu(OTf)_2$, TEMPO, 2,2′-bipy, DBU, MNI;
(*b*) $Cu(OTf)_2$, TEMPO, 3 Å MS, MeCN, 60 °C;
TEMPO is (2,2,6,6-tetramethylpiperidin-1-yl)oxyl,
MNI is *N*-methylimidazole, DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

showed that chiral 2-halomethyl indolines and pyrrolidines (Hal = Cl, Br, I) were formed by $Cu(OTf)_2$-catalyzed oxidative cyclization of alkenes in the presence of 2,2′-methylenebis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] (di-Ph-box) as a chiral catalyst in good yields and enantioselectivities (Scheme 13; for the summary of Cu-catalyzed amination reactions, see Ref. 28).

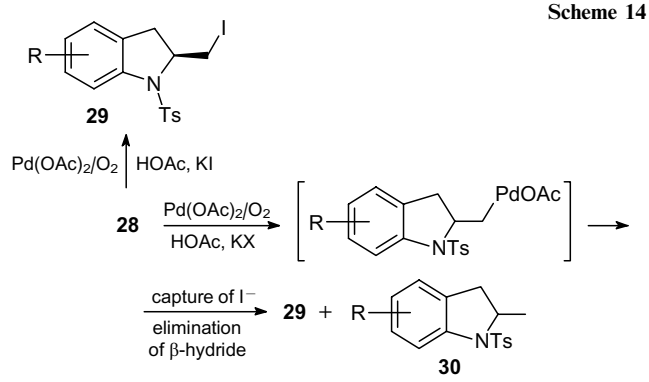
Scheme 13



R = H, 4-Me, 4-CN, 4-F, 3-OMe, 2-OMe, *etc.*;
R′ = Ts, Ns, Ms, *etc.*; Ts = 4-$MeC_6H_4SO_2$,
Ns = 4-$O_2NC_6H_4SO_2$, Ms = $MeSO_2$

Similar reactions were performed using Pd(II) catalyst and molecular oxygen as an oxidant in the presence of potassium halides.[29] Remarkably, the course of the reaction depended on the nature of the salt. While with KI, Pd(II), and KOAc, indolines **29** were formed in up to 95% yields, with other halogens, the β-hydride elimination strongly predominated over the C–X coupling, and in the case of KF, the exclusive formation of *N*-tosyl-2-methylindole **30** in excellent yield was observed (Scheme 14).[29]

Scheme 14

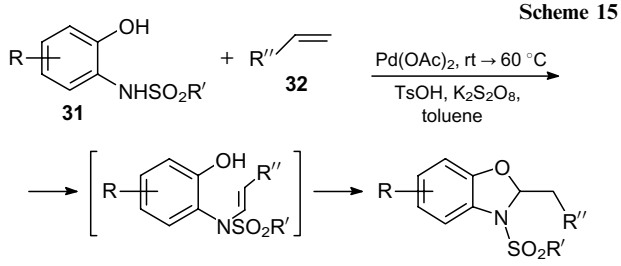


29: R = 7-Me, 6,7-Me_2,
5-OMe, 5-OPh, *etc.*;
30: R = H

X	**29**	**30**
I	to 95%	–
Br	16%	77%
Cl	< 5%	84%
F	–	92%

The $Pd(OAc)_2$-catalyzed reaction of *ortho*-sulfonamidophenols **31** with terminal alkenes **32** using $K_2S_2O_8$ as an oxidant afforded benzoxazoles **33** in moderate to good yields (Scheme 15). If the OH group is separated from the ring by CH_2 group, the corresponding dihydro-1,3-oxazines are formed.[30]

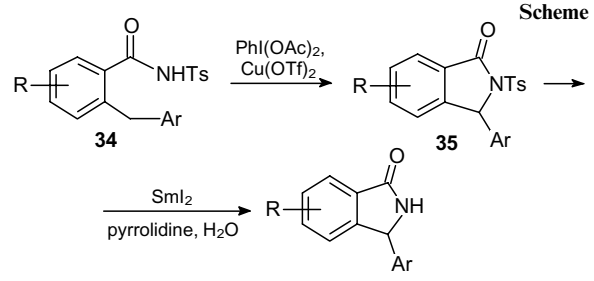
Scheme 15



R = 4-Me, 4-MeC(O), 4-$MeCO_2$, 4-F, 4-Cl, 4-Br;
R′ = 4-$XC_6H_4SO_2$ (X = Me, Et, Cl, Br, MeO), 2,5-$Me_2C_6H_3SO_2$, 2-Th;
R″ = CO_2Me, CO_2Bu, CO_2Bn, Ph, CN, C(O)Ph, C(O)C_6H_4Br-4, OC(O)Ph; Th is thienyl

N-Tosyl 2-benzylated benzamides **34** undergo intramolecular oxidation with $PhI(OAc)_2$ in the presence of $Cu(OTf)_2$ *via* the new C–N bond formation to provide *N*-arylsulfonyl-1-arylisoindolinones **35** (Scheme 16).[31] The latter could be deprotected by SmI_2 to give 1-arylisoindolinones **36**.

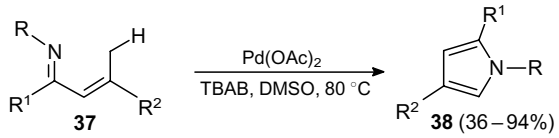
Scheme 16



34: R = 4-Me, 4-OMe, 4-F;
36: Ar = 4-MeC_6H_4 (62%)

Palladium-catalyzed intramolecular amination of the C(sp^3)–H bond in 1-azadienes **37** was proposed as an efficient approach to substituted pyrroles **38** (Scheme 17).[32]

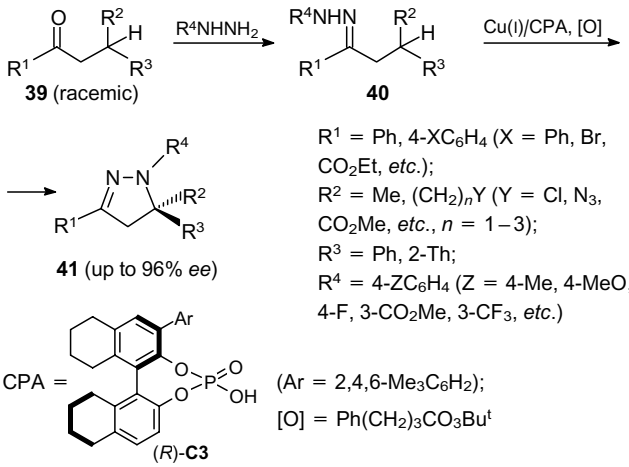
Scheme 17



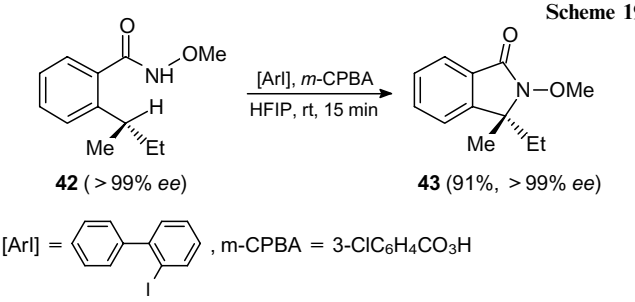
R = Ph, XC_6H_4 (X = 4-Me, 4-OMe, 2-Me), 2-Th, Bu^t;
R^1, R^2 = Ph, YC_6H_4 (Y = 4-Me, 4-Cl, 4-OMe, 3-Br, *etc.*);
TBAB = Bu^n_4NBr

Numerous racemic ketones **39** were cyclized to pyrazolines **41** with high enantioselectivity *via* intermediate hydrazones **40** using Cu(I)/chiral phosphoric acid catalyst (Scheme 18).[33]

Scheme 18



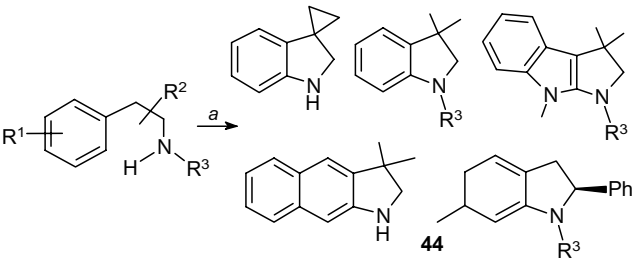
Scheme 19



Even higher retention of enantioselectivity was achieved in the iodoarene-catalyzed heterocyclization of 2-substituted *N*-methoxybenzamides **42** to the corresponding isoindolinones **43** upon oxidation with *m*-CPBA (Scheme 19).[34]

Indolines **44**,[35] as well as indoles and hetero-fused pyrroles[36] were obtained by Cu(II)- or Pd(II)-catalyzed intramolecular CH-activation–heterocyclization, respectively, as exemplified in Scheme 20 for the synthesis of indolines.[35]

Scheme 20

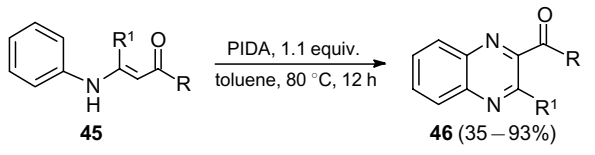


In all cases, the reactions proceeded with the abstraction of hydrogen atoms from the NH group and the C(sp^2)H group of the aromatic ring.

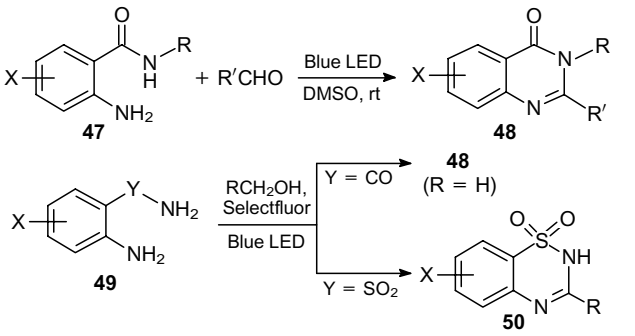
Similar dehydrogenation but involving the vinylic C(sp^2)H group was reported as a straightforward synthesis of quinoxalines **46** from enaminones **45** in up to excellent yields. The reaction was performed in the presence of slight excess of phenyliodine(III) diacetate (PIDA) (Scheme 21).[37]

Using visible light initiation, substituted quinazolinones **48** were obtained in good yields by metal-free oxidative cyclization of 2-aminobenzamides **47** with aldehydes without the need for an additional oxidant (Scheme 22). The driving force of dehydrogenation (possible only for aldehydes[38]) was aromatization of the pyrimidinone ring in quinazolinones **48**. A related process was used for the synthesis of quinazolinones **48** (R = H) and benzothiadiazine *S*,*S*-dioxides **50** using Selectfluor [1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)] in the reaction of the corresponding amides with primary alcohols.[39] The reaction proceeds as hydrogen transfer under the action of Selectfluor™ as a strong oxidant (see Scheme 22).

Scheme 21



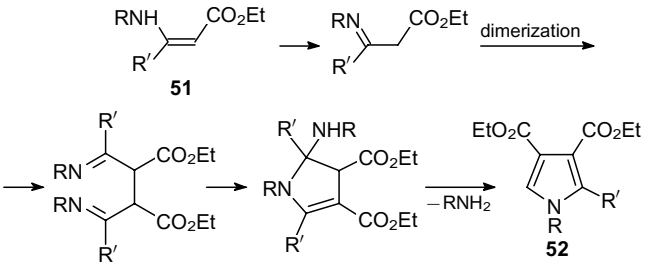
Scheme 22



The importance of quinazolinone heterocycles, which hold a prominent position in drug discovery due to their diverse pharmacological activities, has been highlighted by Khan *et al.*[40]

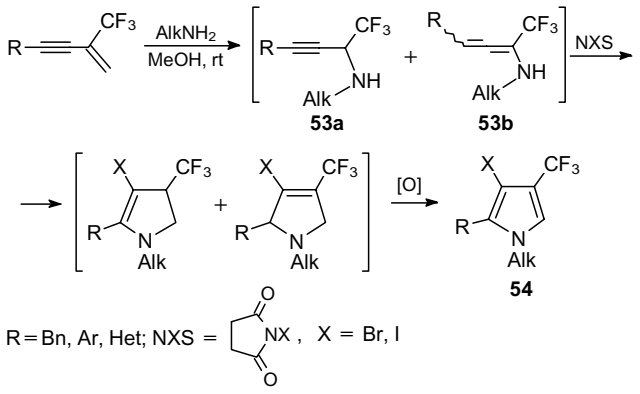
Aromatization was also a driving force in the synthesis of polysubstituted pyrroles **52** from enamines **51** by chemically [$Cu(CF_3COO)_2$, AgOAc, MeCN, O_2;[41] $Cu(OAc)_2$, KOAc, DMSO, O_2 (Ref. 42)] or electrochemically-induced dimerization/cyclization.[43] The reaction mechanism includes enamine–imine isomerization, oxidative C–C coupling, intramolecular cyclization with C–N bond formation, and elimination of amine or ammonia with aromatization (Scheme 23).[43]

Scheme 23



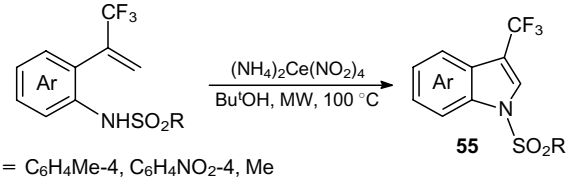
Acetylene–allene isomeric mixture of products **53** of hydroamination of 2-trifluoromethyl-1,3-enynes by primary amines underwent oxidative cyclization to trifluoromethylated pyrroles **54** (Scheme 24).[44] The reaction proceeded under mild reaction conditions with high efficiency.

Scheme 24



N-Sulfonyl-3-(trifluoromethyl)indoles **55** were obtained in up to 88% yield by MW-assisted heterocyclization through the intramolecular C(sp^2)–N bond coupling of α-(trifluoromethyl)styrenes using Ce(IV) as an oxidant. The reaction proceeded *via* SET/dehydrogenation as shown in Scheme 25.[45]

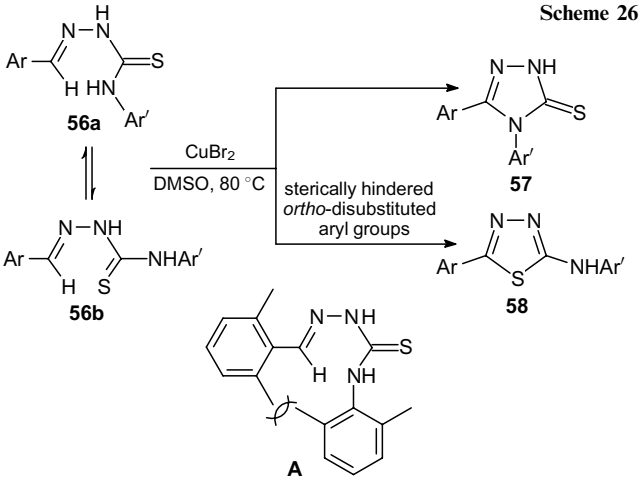
Scheme 25



R = C_6H_4Me-4, $C_6H_4NO_2$-4, Me

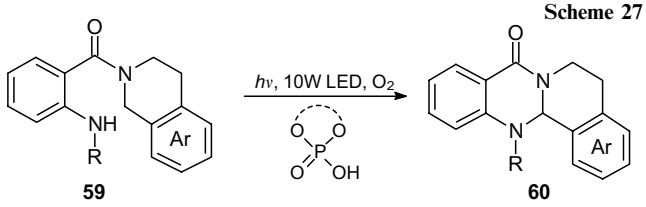
Interesting results were obtained for thiosemicarbazones **56**. Two possible rotamers underwent oxidative intramolecular cyclization with the formation of either C–N or C–S bond to give, respectively, 2,4-dihydro-3*H*-1,2,4-triazole-3-thiones **57** or 2-amino-1,3,4-thiadiazoles **58** (Scheme 26).[46] It was shown that for *meta*- or *para*-substituted Ar groups, the C–N bond formation was preferred in competition with the C–S bond formation, but for di-*ortho*-substituted Ar or Ar′ groups, due to steric repulsion depicted in structure **A** in Scheme 26, the reactivity was reversed and 2-amino-1,3,4-thiadiazoles **58** were formed.

Scheme 26



A visible-light-induced intramolecular C–N cross-coupling reaction of compounds **59** was shown to give N-substituted polycyclic quinazolinone derivatives **60** (Scheme 27).[47] The products were further used for the synthesis of the natural products tryptanthrin, rutaecarpine and their analogues.

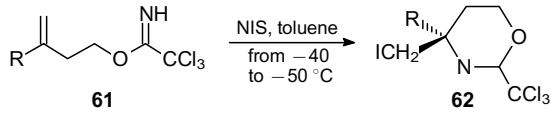
Scheme 27



R = Ph, C_6H_4X (X = 3-CF_3, 3-F, 4-F, 4-CN, *etc.*)

Jacobsen and co-workers[48] carried out an intramolecular oxidative cyclization of trichloroacetimidates **61** in the presence of chiral Schiff base urea derivatives to give 5,6-dihydro-4*H*-1,3-oxazines **62** in up to quantitative yield and with high enantiomeric excess (Scheme 28). Some further transformations of products **62** proceed with retention of the chirality at the quaternary carbon atom.

Scheme 28

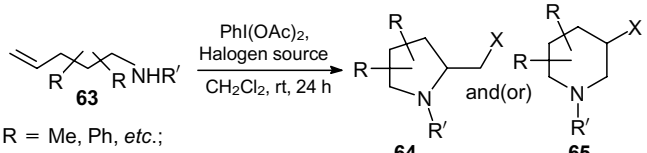


R = Ph, XC_6H_4 (X = 3-F, 4-F, 4-OMe, 4-Ac, 3-Ph, *etc.*) (90–99% *ee*)

A similar strategy was used for intramolecular oxidative halocyclization of alkenes **63** taking advantage of PIDA (Scheme 29).[49] For all halogen sources, the reaction proceeds under mild conditions to afford *N*-tosylpyrrolidines or -piperidines with the halogen atoms in the β-position to the nitrogen atom: 2-(halomethyl)pyrrolidines **64** or 3-halopiperidines **65** in the ratio depending on the substituents in the carbon chain and on the halogen source. As the latter, metal salts, elemental iodine or NIS were used (for I), metal or pyridinium salts (for Br and Cl), and metal or amine salts as well as $BF_3 \cdot Et_2O$ or HBF_4 (for F).

Functionalization of 2-(iodomethyl)-4,4-dimethyl-1-tosylpyrrolidine **64** (X = I) was performed by the reactions with NaN_3, KOAc, *p*-TolSH and phthalimide.[49] Also, the efficiency of other catalysts in haloamination reactions was examined. When treated with $CuCl_2$, *N*-alkyl-2,2-diorganyl-4-pentenylamines **63** gave 5-chloro-1-alkyl-3,3-di-

Scheme 29

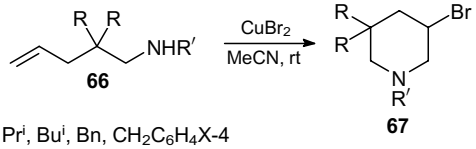


R = Me, Ph, *etc.*;
R′ = Ts, Ms, Ns, Bs;
Bs = $C_6H_4SO_2$

organylpiperidines **65** in good to almost quantitative yields.[50, 51] Note that with $PhCH{=}CHCH_2CPh_2CH_2NHBn$ and $CH_2{=}CH(CH_2)_2CPh_2CH_2NHBn$ as substrates, isomeric products of the pyrrolidine structure similar to that of products **64** (see Scheme 29) were formed.[50] When carrying out the reaction at room temperature, other substrates may also give pyrrolidines in up to 84% yields.[51]

To facilitate further functionalization of 3-chloropiperidines **67** by introduction of a better leaving group, their bromine analogues were synthesized by the reaction of amines **66** with $CuBr_2$ (Scheme 30).[52] Indeed, isomeric 2-(bromomethyl)pyrrolidines were detected but they rearranged into the target piperidines in up to 81% isolated yields. Remarkably, amine $CH_2{=}CHCH_2CPh_2CH_2NHBn$ in the presence of $CuBr_2$ is converted to 3-bromopiperidine, whereas under the same conditions tosylamide $CH_2{=}CHCH_2CPh_2CH_2NHTs$ affords exclusively 2-(bromomethyl)pyrrolidine. Both piperidine and pyrrolidine products readily react with N-, O- and S-nucleophiles to afford the corresponding products of bromine substitution.[52]

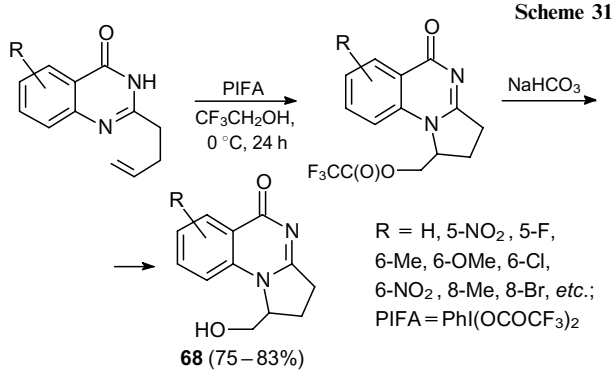
Scheme 30



R = Pr^i, Bu^i, Bn, $CH_2C_6H_4X$-4
(X = NO_2, F, Me, OMe); R′ = H, Ph, $(CH_2)_5$, *etc.*

Recently, the fluorinated analogue of PIDA, phenyliodine(III) bis(trifluoroacetate) (PIFA), was employed for assembling the 2,3-dihydropyrrolo[1,2-*a*]quinazolin-5(1*H*)-one core **68**, a key motif of natural vasicinone alkaloids (Scheme 31).[53]

Scheme 31

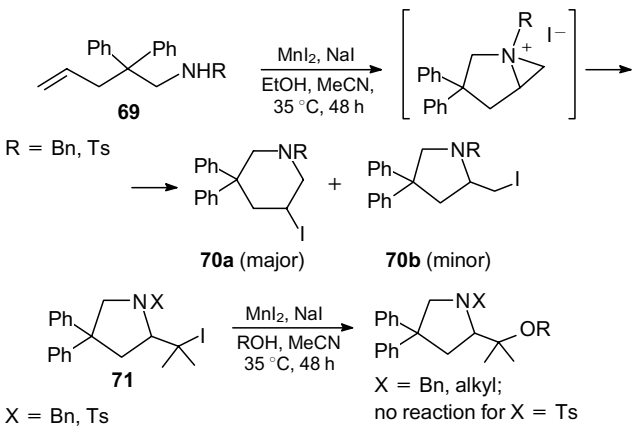


R = H, 5-NO_2, 5-F, 6-Me, 6-OMe, 6-Cl, 6-NO_2, 8-Me, 8-Br, *etc.*;
PIFA = $PhI(OCOCF_3)_2$

MnI_2-catalyzed oxidative aminoiodination of *N*-benzyl- and *N*-tosyl-4-penten-1-amines **69** was shown to give the corresponding 3-iodopiperidines **70a** or 2-iodomethylpyrrolidines **70b** similar to those in Scheme 29 in good to excellent total yield (Scheme 32).[54] Further detailed experiments showed that while the reaction of amines **71** (X = Bn, Alk) with MnI_2 in the presence of alcohol proceeded in good yield, the same reaction with sulfonamide **71** (X = Ts) did not proceed at all.[55]

The probability of formation of the aziridinium intermediate must be higher for the basic NHBn group than for the NHTs group containing much less basic nitrogen atom, so, the failure of the second reaction in Scheme 32 allowed

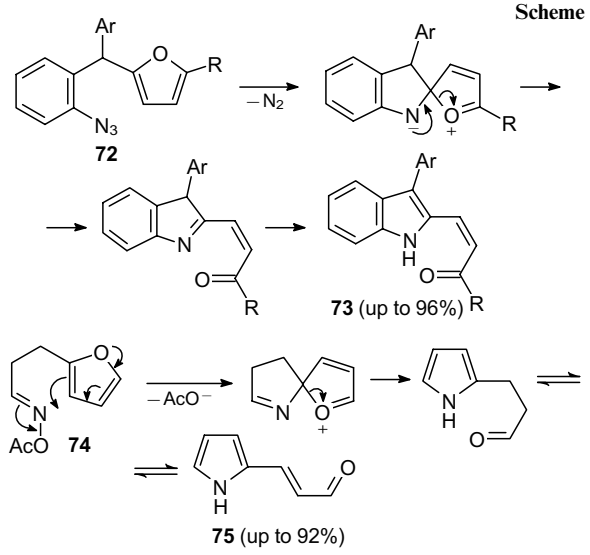
Scheme 32



the authors to rule out an alternative direct replacement of the iodine atom with an alkoxy group.[55]

A conceptually novel approach to the construction of the pyrrole ring, either *per se* or fused to the indole motif was reported by Abaev *et al.*[56] based either on thermolysis of 2-(2-azidobenzyl)furans **72** or on Fe(III)-catalyzed reaction of furans with *O*-acetyl oximes **74**.[57] Both reactions were assumed to proceed *via* spirocyclic intermediates formed by the release of molecular nitrogen from the azide (the first reaction in Scheme 33) or the acetoxy group from O-acetyl oxime (the second reaction in Scheme 33) and the furan ring opening, to afford products **73** and **75**, respectively, in excellent yields.

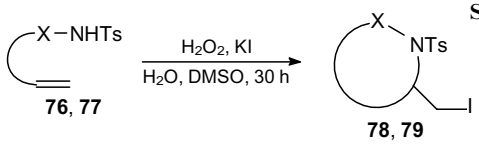
Scheme 33



R = Me, Bu^t, C_6H_4-Cl-4, CH_2Phth (Phth is phthalimido);
Ar = Ph, C_6H_4F-4

Recently, Broggini and co-workers[58] employed a new oxidative system KI/H_2O_2 (30%) in water to produce 4-(iodomethyl)-3-tosyl-1,3-oxazolidin-2-ones **77** from allyl tosylcarbamate and its analogues **76** substituted in the allyl moiety. The same procedure was successfully applied to various unsaturated tosylamines **78** to give 2-(iodomethyl)-4-tosyl-1,2,3,4-tetrahydro-5*H*-1,4-benzodiazepin-5-ones, 3-(iodomethyl)-2-tosyl-3,4-dihydropyrazino[1,2-*a*]-indol-1(2*H*)-ones and 2-(iodomethyl)-1-tosyl-2,3-dihydro-1*H*-indoles **79** (Scheme 34). In a follow-up study, similar reactions were

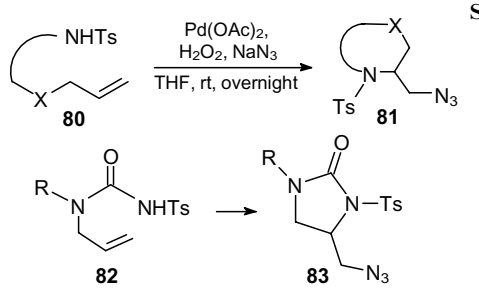
Scheme 34



76, **77** **78**, **79**

X = OC(O) (**76**, **78**), CH_2 (**77**, **79**)

Scheme 35



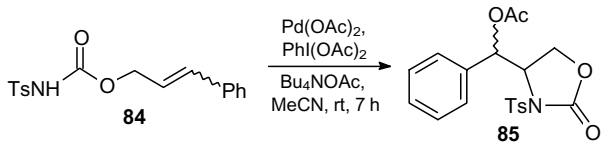
80 **81** **82** **83**

carried out in the presence of sodium azide to provide a convenient protocol for the synthesis of azidomethyl-substituted N-heterocycles **81** and **83**.[59] The reactions proceed under mild conditions and are catalyzed by $Pd(OAc)_2$ to give products **78** in moderate to good yields (Scheme 35).

Note, that the products contain the azide group capable of further transformations. For the substrates **82** with X = amide group, only the products of *N*-cyclization **83** were formed, although O-cyclization involving the amide carbonyl group is also known.

Earlier, high diastereoselectivity (9.5 : 1 or > 20 : 1) of the related cyclization of the *cis*- and *trans*-3-phenylprop-2-en-1-yl tosylcarbamates **84** to 4-[acetoxy(phenyl)methyl]-3-tosyl-1,3-oxazolidin-2-ones **85** was shown (Scheme 36).[60]

Scheme 36

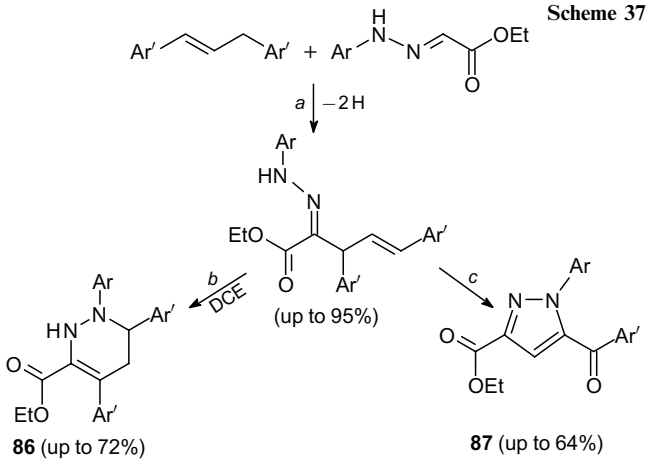


84 **85**

An efficient DDQ-mediated (DDQ is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) one-pot reaction leading selectively to 1,2-dihydropyridazines **86** or pyrazoles **87** under metal-free conditions was reported. The mechanism includes intramolecular cyclization of the intermediate β,γ-unsaturated hydrazones, which further undergo 5-*exo-trig* or 6-*endo-trig* cascade cyclization (Scheme 37).[61]

The reaction of hydrazines with vinyl ketones to give pyrazolines has been known for more than 60 years.[62] Resulting pyrazolines are interesting biologically active compounds, and their chemical stability and biological activity depend on the substituent in the ring. Oxidative aromatization of pyrazolines to pyrazoles[63,64] proceeds easily for H-, Me- or Ar-substituted compounds whereas few methods are known for pyrazolines containing electron-withdrawing groups.[64] At the same time, CF_3-containing pyrazolines might be more stable and may show specific biological activity that prompted elaboration of several approaches to trifluoromethylated pyrazolines, as summarized by Wang *et al.*[65] In the cited work, an efficient method of oxidative cyclization of CF_3-containing homoallylic *N*-acylhydrazines **88** to the corresponding pyrazoline compounds **89** has been developed (Scheme 38). The reaction

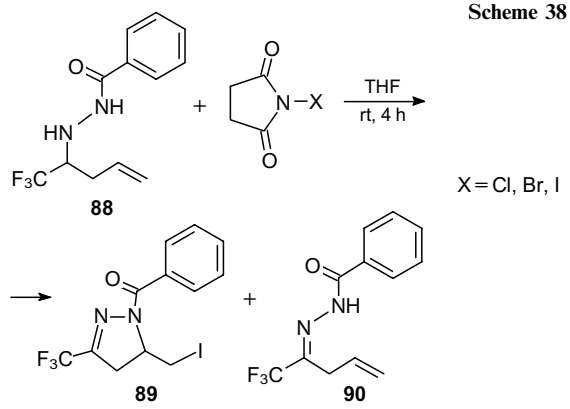
Scheme 37



86 (up to 72%) **87** (up to 64%)

(*a*) DDQ, DCE, 60 °C, 2 h; (*b*) 1) DDQ, 60 °C; 2) I_2, TBHP, O_2, 80 °C, DCE; TBHP = Bu^tOOH; (*c*) 1) DDQ, 60 °C; 2) TBHP, O_2, 80 °C, MeCN; Ar, Ar′ = Ph, C_6H_4R (R = 4-Me, 4-F, 4-Cl, 4-Br, 3-Me, 3,4-Me_2, *etc.*)

Scheme 38



88 **89** **90**

was catalyst-free and proceeded under mild conditions in up to excellent yields.

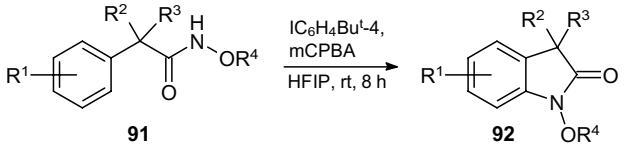
The best yield of **89** (92%, X = I) was achieved for the ratio **88** : NIS = 1 : 4; whereas, when the ratio was 1 : 1 or 1 : 2, the non-cyclized product **90** of oxidation was formed in a moderate yield (41 or 56%), the yield of the target product **89** decreased to 16 or 33%. A strong effect of substituents in the allylic moiety has been revealed: in some cases, the yield of **69** dropped to zero. A plausible mechanism was proposed including N-iodination of **88** with NIS, elimination of HI to give **90**, which reacted with NIS *via* electrophilic iodination of the C=C bond, and the intramolecular cyclization of the iodonium cation to afford, after deprotonation, the target product **89**. The mechanism was confirmed by control experiments, including the reaction of compound **90** with NIS. Pyrazolines **89** were further functionalized through transformation of the halogen atom by the reactions with sodium azide or thiocresolate.

The Ru-catalyzed C–H functionalization with asymmetric allylic alkylation was reported as a route to 3-allyl-3-aryl oxindoles from aryl α-diazoamides.[66]

$N-C_{Ar}$ bond coupling was recently proposed as a mild and efficient synthetic approach to 3,3-disubstituted oxindole derivatives of 1-alkoxy-1,3-dihydro-2*H*-indol-2-ones **92** starting from *N*-alkoxy-2-arylacetamides **91** (Scheme 39).[67]

The reaction on a gram scale gave the products in up to quantitative yield. Note that the amide group enters the intramolecular dehydrogenation reaction *via* the *N*-cycliza-

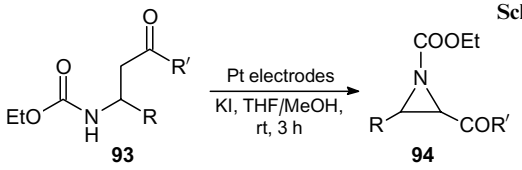
Scheme 39



R^1 = H, 4-Br, 4-Me, 2-F, *etc.*; R^2, R^3 = Me, Et, Ph, $(CH_2)_n$ (n = 2–5), *etc.*; R^4 = Me, Et, Pr^i, Bu^t

tion rather than O-cyclization. There are examples when the intramolecular dehydrogenative coupling of the amide group proceeds on its nitrogen atom, with the carbonyl group remaining intact. For example, ethyl 3-oxocarbamates **93** underwent KI-mediated electrochemical oxidation to aziridines **94** without an external oxidant or metal catalyst in moderate to good yields (Scheme 40).[68]

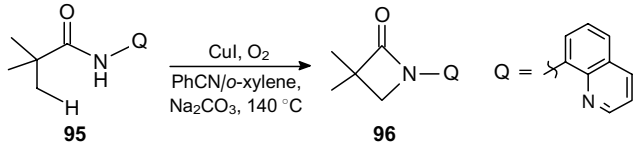
Scheme 40



R = Ph, Ar, C≡CPh; R = Ph, Ar, Het

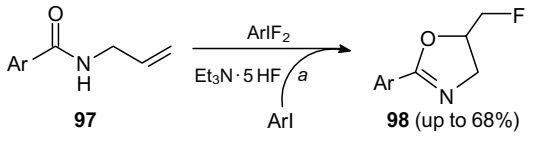
Moreover, a rare case of intramolecular $C(sp^3)-H$ dehydrogenative amidation to produce β-lactams **96** *via* aerobic copper-catalyzed reaction of amides **95** was reported (Scheme 41). Optimization of the reaction conditions allowed increasing the yield to excellent (92%).[69]

Scheme 41



As an alternative to conventional approach of fluorocyclization (see, *e.g.*, Scheme 22 using Selectfluor), Haupt *et al.*[70] proposed an electrochemical generation of usually poorly stable difluoroiodoarenes and their reaction with *N*-allylbenzamides **97** to afford 1,3-oxazolines **98** in moderate yields (Scheme 42).

Scheme 42

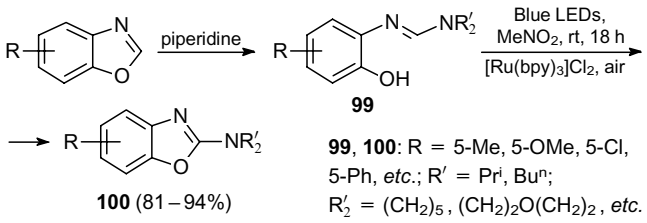


(*a*) Pt || Pt undivided cell, CH_2Cl_2, 5–15 h; Ar = Ph, C_6H_4R (R = 4-Me, 4-Bu^t, 4-OMe, 4-CF_3, 4-Cl, 3-Cl, 2-Cl, 2-Br), *etc.*

2.3. C–O bond coupling

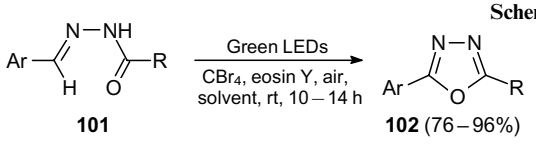
Cyclization *via* dehydrogenative C–O bond formation can lead to N-heterocycles provided that the nitrogen-containing group is already present in the molecule in at least one of the coupled fragments. Thus, the environmentally benign $[Ru(bpy)_3]Cl_2$-catalyzed oxidation of *ortho*-phenolic amidines **99** (obtained by the piperidine-induced ring opening of benzoxazoles)[71] with molecular oxygen afforded 2-aminobenzoxazole derivatives **100** in excellent yields (Scheme 43).[72] Simultaneous action of the photocatalyst, air, and visible light was essential for the reaction.

Scheme 43



Using the same strategy, Yadav and co-workers[73,74] elaborated an efficient method for the synthesis of 1,3,4-oxadiazoles **102** by aerobic oxidative cyclization of semicarbazones **101** using CBr_4 as a source of bromine, eosin Y as a catalyst, and visible light irradiation (Scheme 44). The yields of target products **102** reached excellent values.

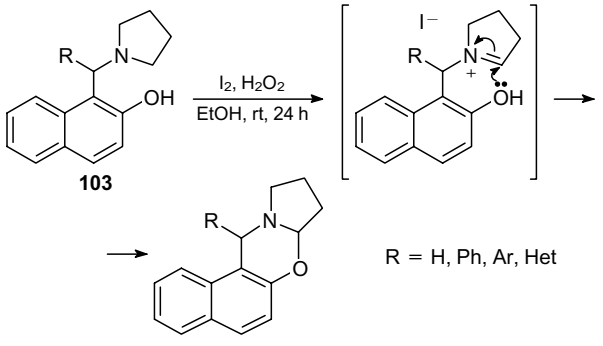
Scheme 44



Ar = Ph, C_6H_4X (X = 4-Me, 4-OMe, 4-Br, 4-NO_2, 3-NO_2); R = Ph (solvent = DMF), NH_2 (solvent = CBr_4).

The search for transition metal-free protocol for assembling new structures **104** containing the [1,3]-oxazine motif as bioactive compounds, resulted in the development of an environmentally benign method based on the iodine-catalyzed intramolecular cross-dehydrogenative C–O coupling using H_2O_2 as an oxidant and ethanol as a solvent (Scheme 45).[75]

Scheme 45

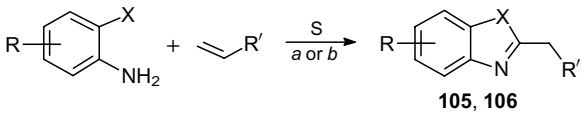


The yields of [1,3]-oxazines **104** vary from good to excellent. A tentative mechanism includes the NCH proton abstraction by the intermediate hypoiodous acid (HOI) to give the iminium iodide salt, tautomerization with migration of the C=N bond into the ring, and nucleophilic

attack of the oxygen lone pair on the iminium carbon with the ring closure.

Elemental sulfur was used as a mild oxidant in assembling benzoxazole and benzothiazole skeletons from *ortho*-aminophenols and *ortho*-iodoanilines.[76] The optimized isolated yields of compounds **105**, **106** reached excellent values on heating to 130 °C in *N*-methylpiperidine or DMF (Scheme 46).

Scheme 46



105, **106**

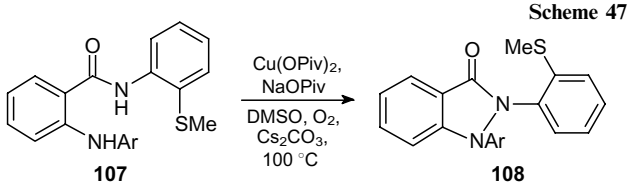
(*a*) X = O, *N*-methylpiperidine, 110 °C, 36 h;
(*b*) X = S, $CuCl_2 \cdot 2H_2O$, 1,10-phenanthroline, K_2HPO_4, DMF, 130 °C, 12 h; X = OH, I; R = H, 4-Cl, 4-Me; R′ = Ph, C_6H_4X (X = 4-Cl, 4-Br, 4-Me, 4-OMe, 2-Cl, 3-Me), *etc.*; X = O (**105**), S (**106**)

The fact that the reaction proceeded as a sulfur-mediated process even for aminophenols was evidenced by the failure of the formation of benzoxazoles **105** in the absence of sulfur. The plausible mechanism included sulfurization of the NH_2 group, addition to alkene, dehydrogenation and nucleophilic addition of the second aniline molecule, followed by an intramolecular cyclization and conversion to the final product assuming that sulfur was the sole oxidant in the system.[76]

2.4. N–N and N–S bond coupling

The oxidative N–N bond formation accompanied by cyclization has been used to assemble various *N*-heterocycles, such as tetrazoles,[77] pyrazoles,[78] 5-amino-1,2,4-thiadiazoles,[79] indazoles,[80,81] indazol-3-ones[82] or 1,2,4-triazoles.[83] For example, 2-anilino-*N*-(2-methylthiophenyl)-benzamides **107** formed by Cu(II)-mediated amination of the corresponding benzamides underwent intramolecular dehydrogenative N–N bond coupling to afford indazol-3-ones **108** in moderate to good yields (Scheme 47).[82]

Scheme 47

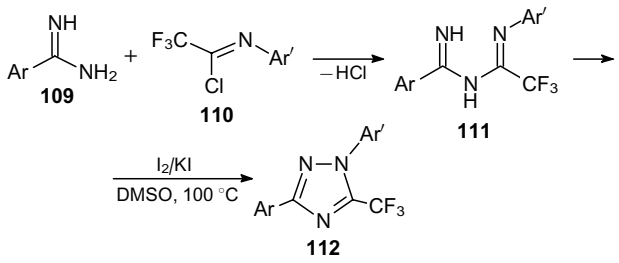


107 **108**

Piv = Bu^{t}C(O)

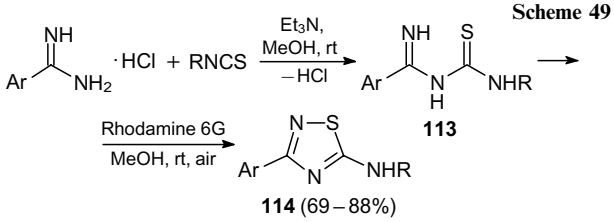
Kazemi and Darehkordi,[83] motivated by the pronounced biological activity of 1,2,4-triazole derivatives, proposed an efficient method for the synthesis of 5-trifluoromethylated triazoles **112** in excellent yields by intramolecular oxidative cyclization of the corresponding condensation products **111** of benzimidamides **109** with imidoyl chlorides **110** (Scheme 48).

Scheme 48



When the NCNCN pentad in **111** is replaced by the NCNCS pentad, 1,2,4-thiadiazoles should be formed. Indeed, an efficient one-pot metal-free protocol for the synthesis of these compounds under mild conditions and in excellent yield *via* the oxidative N–S bond formation has been developed using molecular oxygen as a green oxidant and Rhodamine 6G as a photocatalyst. The precursors of the target heterocycles, *N*-(arylcarbamothioyl)imidamides **113**, are easily obtained from amidines and isothiocyanates and undergo intramolecular cyclization to the target 3-substituted 5-amino-1,2,4-thiadiazoles **114** (Scheme 49).[79,84]

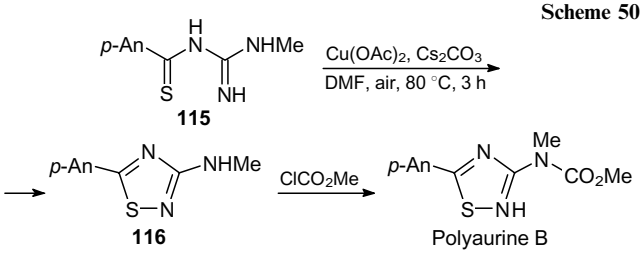
Scheme 49



R = Ph; XC_6H_4 (X = 4-Me, 4-OMe, 4-F, 3-Me, 3-Cl, *etc.*)

If to swap the aryl and methylamino groups in compounds **113**, the resulting thioacylguanidines **115** are also capable of oxidative heterocyclization as shown in Scheme 50 by the example of the synthesis of alkaloid polyaurine B containing 1,2,4-thiadiazole ring *via* isolated intermediate **116**.[85] Cyclization to **116** proceeds under the action of $Cu(OAc)_2$.

Scheme 50

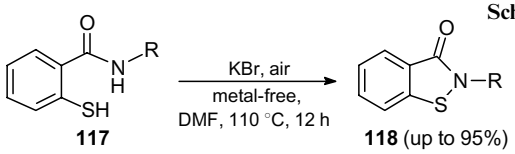


p-An = C_6H_4OMe-4

Also, Cu-induced oxidation was used to obtain 3-amino-5-acyl-1,2,4-thiadiazole core of polycarpathiamines, as an alternative to dipolar addition providing poor yields.[86]

Disubstituted amidines ArNRC(=NH)Ar′ undergo electrochemical oxidative intramolecular cyclization to benzimidazoles in moderate yields.[87] In an earlier study,[88] the strategy based on the N–S bond formation was proposed for the synthesis of 2-substituted 1,2-benzisothiazol-3(2*H*)-ones **118** from 2-mercaptobenzamides **117** as a metal-free

Scheme 51



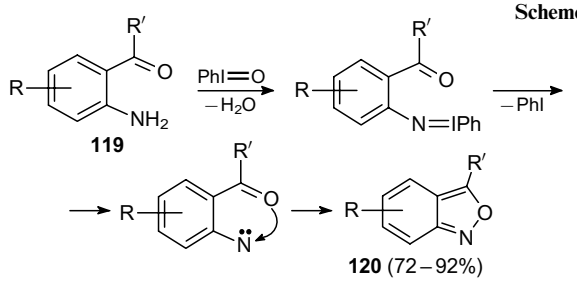
R = C_6H_4X-4 (X = Me, OMe, Cl, Br, *etc.*), $C_6H_2(Br)_3$-2,4,6, Naph, Bn, cyclo-C_3H_5, cyclo-C_6H_{11}, *etc.*

alternative approach taking advantage of using a cheap catalyst (KBr) and a green oxidant (air) (Scheme 51).

Most of studies on oxidative *intermolecular* coupling reactions were summarized in a mini-review [89] and will not be considered here.

Oxygen analogues of compounds **118**, 2,1-benzisoxazoles (anthranils), are well known and can be synthesized by numerous methods, including intramolecular oxidative heterocyclization using oxone $KHSO_5$ as an oxidant.[90,91] Recently, a catalyst-free synthesis of anthranils **120** from *ortho*-acylanilines **119** under mild conditions using iodosobenzene as an oxidant was reported.[92] The reaction tolerates a broad scope of substrates and the yields, depending on solvent, may reach excellent values. The mechanism, confirmed by control experiments, includes oxidation of the amino to iminoiodinane group (−N=IPh), which eliminates iodobenzene, and the generated nitrene is attacked by the oxygen lone electron pair to form the O−N bond (Scheme 52).

Scheme 52



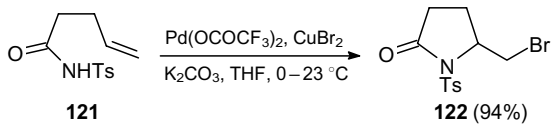
R′ = Ph, XC_6H_4 (X = 3-F, 4-Cl, 4-Br, 4-NO_2, 5-Cl, 5-Me);
R′ = Ph, YC_6H_4 (Y = 2-Me, 3-Me, 4-F, 4-OBn), *etc.*

3. Intramolecular heterocyclization *via* dehydrohalogenative C−N bond coupling ‡

For almost all the above-mentioned reactions, the oxidation occurs in the stage of heterocyclization, that is, during the coupling of the C−C, C−heteroatom, or heteroatom−heteroatom bonds resulting in the formation of a heterocycle. However, there is another type of reactions affording N-heterocycles, in which an external oxidant (usually a source of an electrophilic halogen) activates an aminating reagent which adds to an unsaturated substrate, and in the next step, heterocyclization occurs *via* intramolecular dehydrohalogenation. The intermediate adducts can be isolated or, sometimes, the reaction proceeds in one synthetic step and can be performed in a one-pot manner. Most of the reactions of this type published until 2018 were considered in our recent reviews,[1,2] so in the present Section we will focus on the most recent works published over the last 3−4 years. Even in the absence of an external oxidant, the reactions of unsaturated substrates with pre-oxidized aminating reagents (*e.g.*, RSO_2NCl_2) can be considered as oxidative heterocyclization, so they will also be briefly mentioned in this Section.

Prior to our studies, only two examples of oxidative intramolecular bromosulfamidation have been known. The first was the aforecited Pd(II)-catalyzed intramolecular aminohalogenation of olefins using a stoichiometric amount of Cu(II) halides to facilitate halogen transfer and catalyst oxidation.[26] The reactions proceeded in excellent yields as exemplified in Scheme 53 for the synthesis of 5-(bromomethyl)-1-tosylpyrrolidin-2-one **122** from *N*-tosylpent-4-enamide **121**.

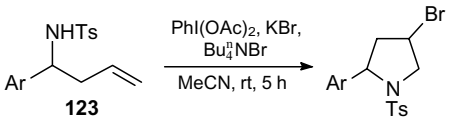
Scheme 53



121 **122** (94%)

The second example was the cyclization of homoallylic arylsulfonamides **123** into 2-aryl-4-bromopyrrolidines **124** with $PhI(OAc)_2$ as an oxidant and KBr as a bromine source (Scheme 54).[93]

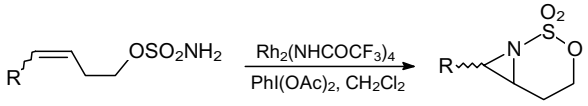
Scheme 54



123
124 (71–92%)

As to intramolecular sulfamidation of unsaturated silanes, it was virtually unexplored until our studies, not to mention the synthesis of N-heterocycles on this basis. The Rh-catalyzed oxidative sulfamidation of 4-silylated sulfamates **125** could be noted as the only exception (Scheme 55).[94]

Scheme 55



125
126 (62–92%)

R = H, Ph, $SiMe_3$, $SiPh_3$, CO_2Bu^t, P(O)OEt_2, C≡C$SiPr^i_3$

The diastereoselectivity of aziridination depends on the nature of R and the configuration of the double bond. Thus, for R = Ph-*trans*, the hydrogen atoms of the aziridine ring were shown to be in the *trans*-position, whereas for R = Ph_3Si-*cis*, they are in the *cis*-position to each other.[94]

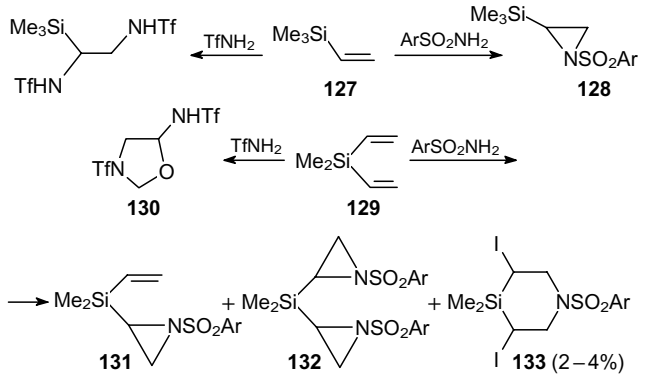
At the same time, vinylsilanes should be reactive substrates in electrophilic sulfamidation due to the stabilizing effect of the silicon atom on β-carbocations. In the first report on this matter, reactions of vinylsilanes **127**, **129** with sulfonamides were studied (Scheme 56).[95]

As is evident from Scheme 56, the reactions of triflamide and arenesulfonamides are quite different. With the latter, aziridines **128**, **131**, **132** were the major products, whereas, unexpectedly, non-silylated oxazolidine **130** was formed with triflamide. The same product was also formed in the reaction of $TfNH_2$ with diphenyl(divinyl)silane. The proposed mechanism included the rupture of the Si−C(sp^2) and C=C bonds to give oxazolidine **130**.[95]

The use of NBS as the oxidant changes the reaction course, and it becomes strongly solvent-dependent.[96] In CH_2Cl_2, silane **127** reacts with sulfonamides to give the products of bromosulfamidation **134** in up to excellent

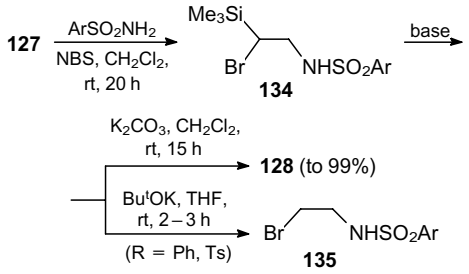
‡ Based partly on the author's lecture at the KOST-2021 International Congress on the Chemistry of Heterocyclic Compounds (October 12–16, 2021, Sochi, Russian Federation).

Scheme 56



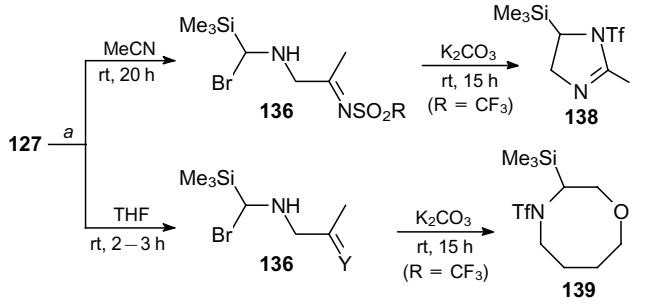
yields; the latter undergo base-catalyzed dehydrobromination to aziridines **128** in up to quantitative yield. However, for $PhSO_2NH_2$ or $TsNH_2$, and Bu^tOK as a base, desilylation to *N*-(2-bromoethyl)arenesulfonamides **135** occurs in quantitative yield due to high oxophilicity of silicon with respect to very strong base (Scheme 57).

Scheme 57



Sulfamidation of silane **127** in MeCN or THF proceeded with solvent interception to give bromoamidine **136** or *N*-(4-[2-bromo-2-(trimethylsilyl)ethoxy]butyl)sulfonamides **137**, which in the case of $R = CF_3$ underwent dehydrobromination to imidazoline **138** or 1,4-oxazocane **139** with yields close to quantitative (Scheme 58).[96] Note that insertion of cyclic ethers into the products of the NBS-induced reaction of olefins with nosylamide has been reported earlier.[97]

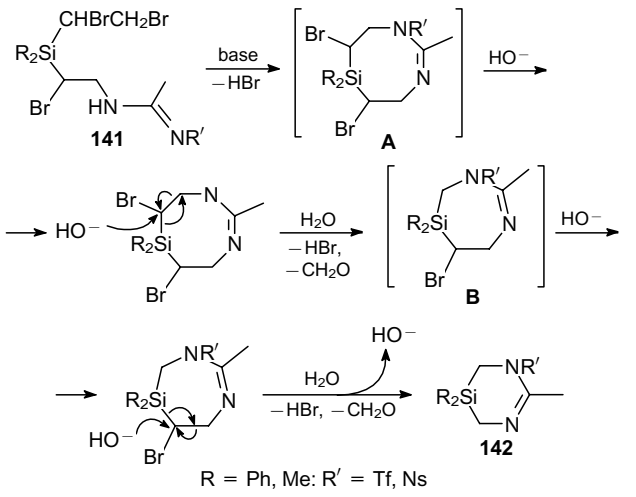
Scheme 58



(*a*) RSO_2NH_2, NBS; R = Me, CF_3, 4-C_6H_4X (X = Me, Cl, Br, OMe, NO_2); Y = $O(CH_2)_4NHSO_2R$

The reactions of diphenyl(divinyl)silane **140**, as an analogue of **129**, with a series of sulfonamides in the presence of a series of oxidants in various solvents were studied.[98] Most of the heterocyclization reactions were similar to those as illustrated in Schemes 56, 58, differing by the presence of the R_2Si(vinyl) substituent in the molecule (R = Me, Ph). However, a remarkable finding was the formation of a new type of heterocycle, namely, 1,3,5-diazasilinanes **142**, in almost quantitative yields by the reaction of compounds **141** (products of bromination at one C=C bond and bromoamination with solvent interception at the other one) with K_2CO_3. The only currently known six-membered heterocycles with one silicon and two nitrogen atoms in the ring were 1,4,2-diazasilinanes prepared by the insertion of N-heterocyclic carbenes (NHC) into the Si–H bond[99] (for a minireview on the use of NHC in the synthesis of heterocycles *via* oxidative cyclization see Ref. 100). A tentative mechanism is shown in Scheme 59. The reaction begins with the formation of intermediate **A**, which undergoes two nucleophilic attacks on the CHBr groups with the Si–CHBr / Si–CH_2 formation/C–CHBr cleavage.

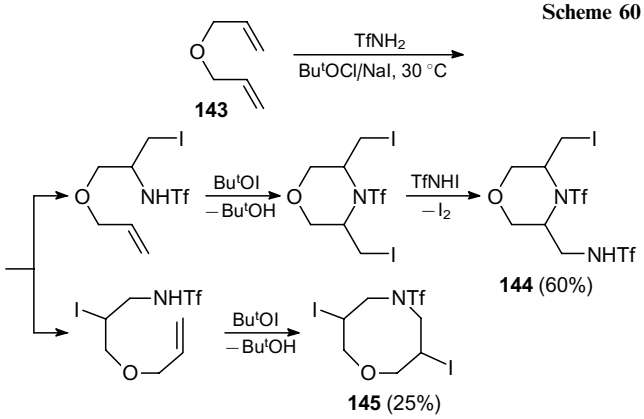
Scheme 59



R = Ph, Me: R′ = Tf, Ns

The aforementioned specific behaviour of triflamide and the products thereof prompted us to examine its reactions with allylic substrates, including allyl ethers, amines and silanes under oxidative conditions.[101] Earlier, we have shown that allylic substrates may exhibit unusual reactivity towards triflamide, *e.g.*, to afford the first acyclic λ^4-sulfane by oxidation of the sulfur atom.[102] As applied to the topic of the present review, the formation of two heterocycles, 3-iodomethyl-4-triflyl-5-(triflamidomethyl)morpholine **144** and 3,7-diiodo-5-triflyl-1,5-oxazocane **145** in the reaction of diallyl ether **143** with triflamide in the presence of

Scheme 60



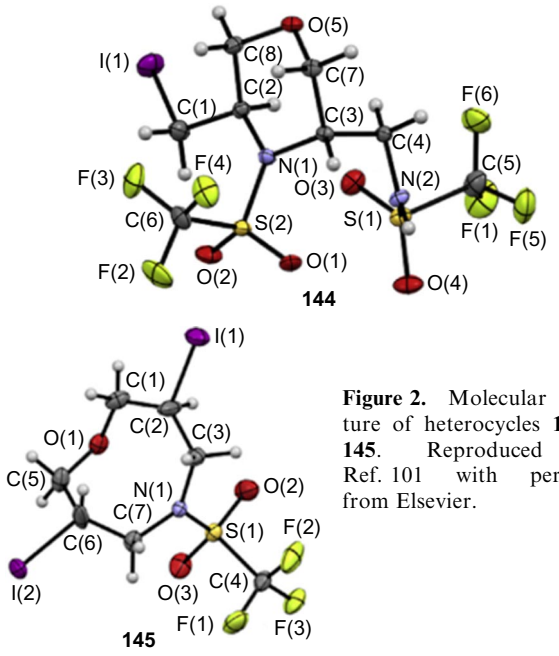


Figure 2. Molecular structure of heterocycles **144** and **145**. Reproduced from Ref. 101 with permission from Elsevier.

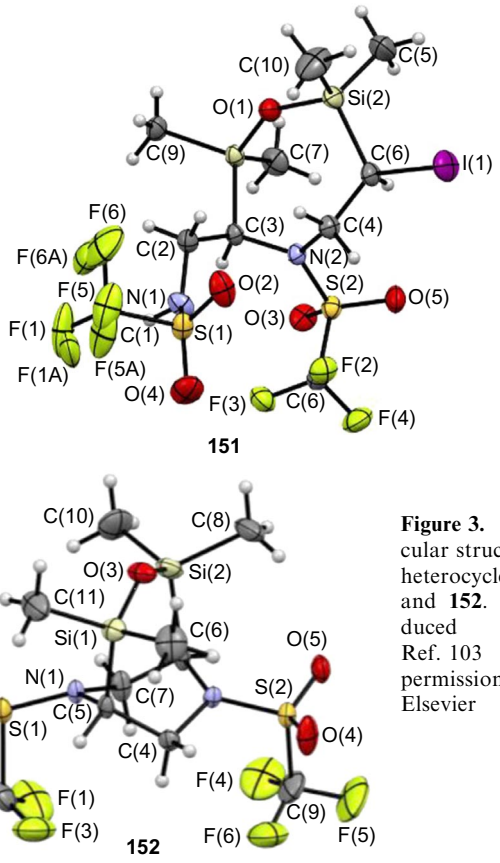
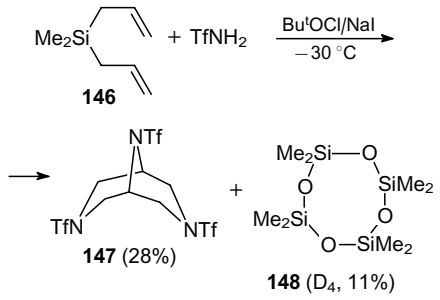


Figure 3. Molecular structure of heterocycles **151** and **152**. Reproduced from Ref. 103 with permission from Elsevier

Bu^{t}OCl/NaI should be mentioned (Scheme 60). The structure of both compounds was confirmed by X-ray diffraction analysis (Fig. 2).[101]

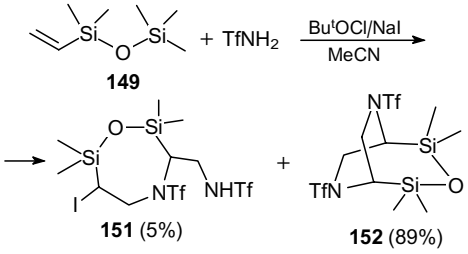
Diallylsilane **146** reacted with triflamide *via* desilylation to give bicyclic N-heterocycle **147**, accompanied by elimination of siloxane D_4 **148** (Scheme 61).[101]

Scheme 61



New heterocycles were also synthesized by oxidative sulfamidation of siloxane **149** and (allyloxy)trimethylsilane **150**.[103] Siloxane **149** with two terminal C=C double bonds can be considered as a heteroatomic homologue of hexa-1,5-diene, which was shown to react with sulfonamides in the system Bu^{t}OCl–NaI to afford 2,5-bis(iodomethyl)-*N*-sulfonylpyrrolidines and, in the case of triflamide, 3,8-bis(triflyl)-3,8-diazabicyclo[3.2.1]octane.[104] The formation of the latter was the first and at that time the only example

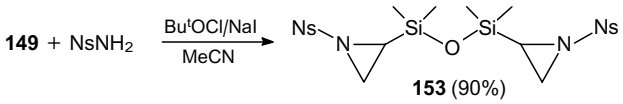
Scheme 62



of one-pot assembling of such heterocycles. With triflamide, siloxane **149** gave two heterocycles in excellent total yield: 6-iodo-3-(triflamidomethyl)-4-triflyl-1,4,2,7-oxazadisilepane **151** (minor) and 2,2,4,4-tetramethyl-6,8-bis(triflyl)-3-oxa-6,8-diaza-2,4-disilabicyclo[3.2.2]nonane **152** (major) (Scheme 62, Fig. 3).[103]

As distinct of that, nosylamide reacts with siloxane **149** under the same conditions to afford diaziridine **153** in excellent yield (90%) due to its lower NH acidity with respect to $TfNH_2$ (Scheme 63).[103]

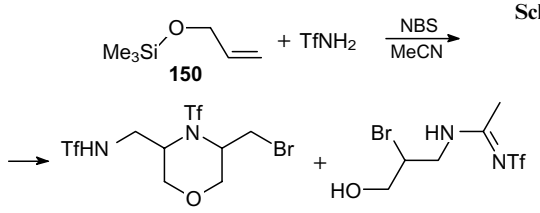
Scheme 63



When NBS was used as an oxidant, no heterocycles were formed; both $TfNH_2$ and $NsNH_2$ reacted with siloxane **149** to give linear Ritter-type products of bromosulfamidation. However, triflamide reacts with (allyloxy)trimethylsilane **150** in the presence of NBS *via* desilylation/heterocyclization to afford substituted morpholine **154** and amidine **155** in quantitative total yield (Scheme 64).[103]

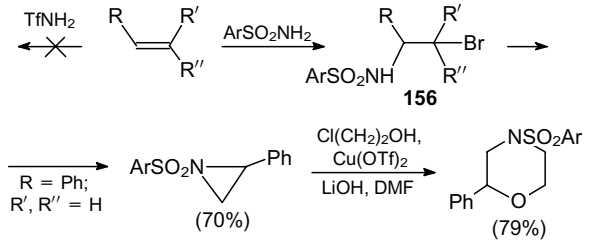
Strange as it might seem, the first work on catalyst-free and metal-free bromoamidation of alkenes appeared as late as in 2015.[105] Earlier, the NBS-induced catalyst-free reaction of styrene with tosylamide was shown to provide a mixture of regioisomers in a poor yield (20%).[106] The use of different metal salts allowed researchers to guide the reaction selectively to a specific regioisomer. The reactions of arenesulfonamides with styrene as a model compound in the

Scheme 64



presence of NBS in CH_2Cl_2 gave the products of bromosulfamidation **156**, but the reaction with triflamide under the same conditions failed (Scheme 65).[105] As to heterocyclization, the authors succeeded in preparation of *N*-(*p*-trifluoromethylphenylsulfonyl)phenylaziridine, which underwent the ring opening/ring closure sequence with 2-chloroethanol to give 2-phenylmorpholine.[105]

Scheme 65

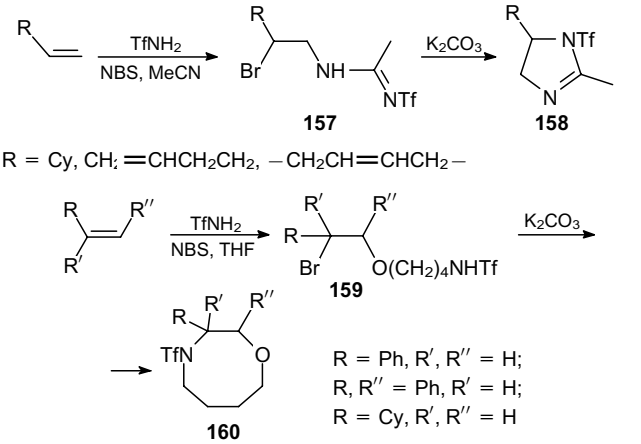


R = Ar, Alk; R′, R″ = H, Alk; conditions: NBS, CH_2Cl_2, 26 °C, 24 h

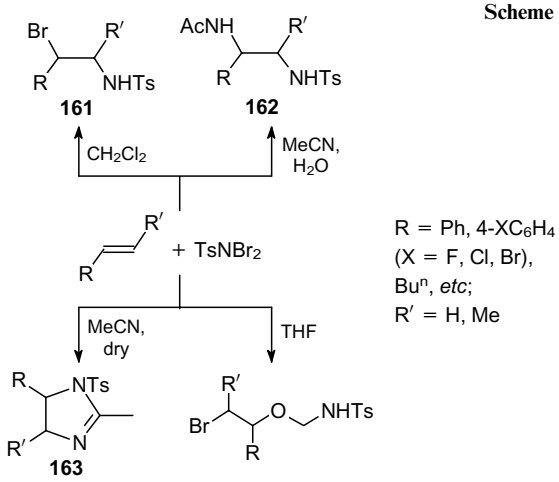
At the same time, a series of unsaturated silanes were successfully subjected to halotriflamidation and heterocyclization in various oxidative systems (*vide supra*). To fill in this gap, we studied triflamidation of alkenes in the presence of various oxidative systems and solvents and found them to furnish the products of the amidine and acetamide types.[107] For example, using NBS in MeCN or THF, the solvent interception products of bromotriflamidation **157** and **159** were formed, which underwent base-induced intramolecular heterocyclization to 1*H*-imidazolines **158** and 1,4-oxazocanes **160** under mild conditions in practically quantitative yield (Scheme 66, *cf*. Scheme 58).

In the absence of an external oxidant, oxidative haloamidation can still be performed by using pre-oxidized aminating reagents such as *N*,*N*-dihalosulfonamides. Thus, Rajbongshi *et al*.[108] studied the reactions of a series of linear

Scheme 66



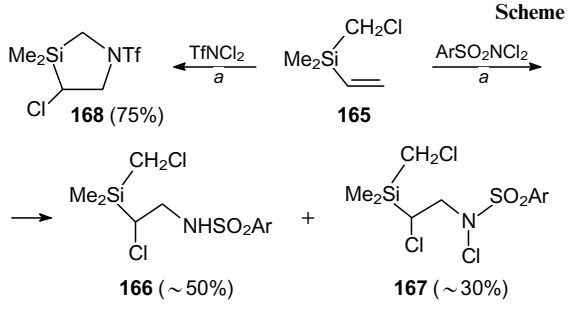
Scheme 67



and cyclic alkenes including substituted styrenes with *N*,*N*-dibromotosylamide. The course of the reaction strongly depended on the solvent (Scheme 67). In methylene chloride, which is incapable of being captured by any intermediate formed during the reaction, only the products of bromosulfamidation **161** were obtained (*cf*. adducts **134** in Scheme 57 and **156** in Scheme 65). Linear compound **162** having the structure of the bis-amidation product with the acetamide residue instead of bromine is formed in aqueous acetonitrile. In contrast, in an anhydrous solvent, imidazolines **163** similar to **138** (see Scheme 58) and **158** (see Scheme 66) were formed, apparently, *via* intramolecular cyclization of the intermediate Ritter type products of the solvent (MeCN) interception. The products **164** of solvent interception were also generated in THF, which underwent ring opening, although they did not cyclize into 1,4-oxazocanes, like similar solvent interception products **137** (see Scheme 58) and **159** (see Scheme 51).

We have first studied the reactions of *N*,*N*-dichlorotriflamide with vinylsilanes. In the case of trimethylvinyl-, dimethyl(divinyl)- and diphenyl(divinyl)silanes, only products of chlorotriflamidation at one or two bonds were obtained.[109] In a similar manner, that is, by exclusive addition to the double bond, chloromethyl(dimethyl)vinylsilane **165** reacted with (*N*,*N*-dichloro)arenesulfonamides to give linear adducts **166** and **167**. However, the reaction of silane **165** with $TfNCl_2$ proceeded as heterocyclization to give 4-chloro-3,3-dimethyl-1-triflyl-1,3-azasilolidine, apparently, due to much higher NH acidity of the TfNH group in the intermediate compound analogous to **166** in Scheme 68.[110]

Scheme 68



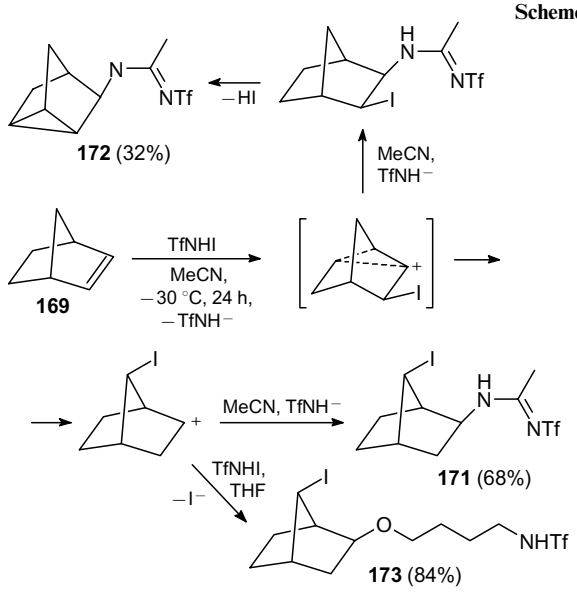
(*a*) CCl_4, −10 → 20 °C, 2–3 h; Ar = 4-RC_6H_4 (R = Me, Cl)

The synthesis of 1,3-azasilolidine **168** was named as 'Shainyan's synthesis' in the recent review[111] on the synthesis of 5- and 6-membered silaazacycles, which described a number of other schemes for the design of the title compounds, including oxidative cyclizations.

To address a challenging question about the specific reactivity of triflamide, which has repeatedly been mentioned, *vs* nonfluorinated sulfonamides, a quantum chemical analysis of the Bu^{t}OI-induced oxidative sulfamidation of a series of substrates and reagents was performed at a high level of theory and taking into account the solvent effect.[112] The newly formed active intermediate Bu^{t}OI generates mono- and diiodinated amides RSO_2NHI and RSO_2NI_2. The iodinating activity increases in the series RSO_2: Ts ⩽ Ms < Ns ≪ Tf being higher for RSO_2NI_2 than for RSO_2NHI. The intriguing difference between the reactivity of triflamide providing mainly bis-triflamidation products and non-fluorinated sulfonamides leading to aziridines is due to different thermodynamics of these two routes. The preference of addition over cyclization caused by a high strain of the aziridine ring is 3.1 kcal mol^{-1} higher for triflamide than for mesylamide. Smaller entropy loss for triflamide increases this difference to 4.2 kcal mol^{-1}, thus explaining the experimental results. The mechanism of the reaction of non-fluorinated sulfonamides with divinylsilanes **129** and **140** revealed that the reaction gives *N*-sulfonylaziridines and 1,4-azasilinanes as the kinetic and thermodynamic products, respectively.[112]

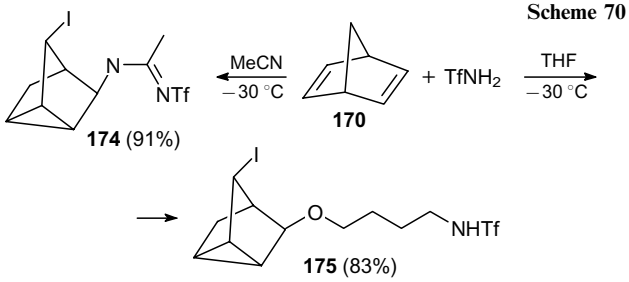
An interesting example of oxidative cyclization was found when studying the reaction of norbornene **169** and norbornadiene **170** with triflamide using Bu^{t}OCl-NaI or NXS (X = Br, I) as oxidants in MeCN or THF media.[113] With norbornene and Bu^{t}OCl-NaI in MeCN, triflamide gave (2*S*,7*R*)-*N*-(7-iodobicyclo[2.2.1]heptane-2-yl)-*N*′-(triflyl)acetamidine **171** (rather than its 2-iodo-substituted isomer expected from simple iodotriflamidation of the double bond) and *N*-tricyclo[2.2.1.0^{2,6}]hept-3-yl-*N*′-(triflyl)acetamidine **172** in quantitative total yield. Product **171** is formed *via* skeletal rearrangements, though not leading to heterocyclic compounds. Tricyclic compound **172**, which was formally the product of dehydroiodination, could not arise from elimination of HI from **172**. In THF, *N*-(4-(3-iodobicyclo[2.2.1]heptan-2-yloxy)butyl)triflamide **173** was obtained in a very good yield (84%). A tentative mechanism is depicted in Scheme 69.

Scheme 69



In the same oxidative system, norbornadiene **170** gave *N*-(5-iodotricyclo[2.2.1.0^{2,6}]heptane-3-yl)-*N*′-(triflyl)acetamidine **174** (which is the 7-iodo analogue of compound **172**) in excellent yield. In THF, the tricyclic product **175** (analogue of compound **173**) was obtained in a very good yield (Scheme 70).

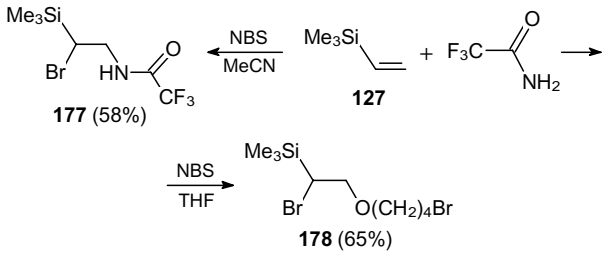
Scheme 70



In going to NBS and NIS as oxidants, the same products as in Schemes 69, 70 were obtained, except that the ratio of the diastereomers with different configuration at the C(7) atom differed from that in the system Bu^{t}OCl−NaI as well as from each other for NBS and NIS.[113]

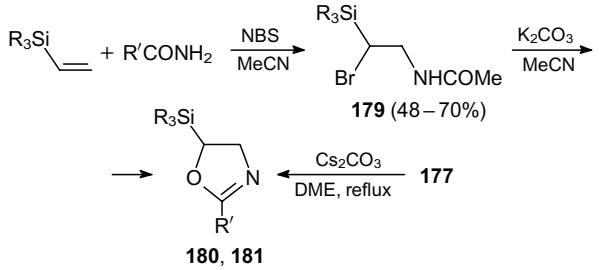
Unlike reactions of sulfonamides with alkenes leading to aziridines,[114] typical reaction of carboxamides is haloamination.[115–118] However, trifluoroacetamide reacted differently from non-fluorinated amides resulting in a wide variety of products, including heterocycles.[119–122] Silanes **127**, **129**, **140**, and triphenyl(vinyl)silane **176** reacted with acetamide and benzamide in the system Bu^{t}OCl/NaI to afford halogenation products, and only with CF_3CONH_2, silanes **127** and **129** gave iodotrifluoroacetamidation products.[123] Reacting with NBS, silane **127** afforded dibromide $Me_3SiCHBrCH_2Br$ in CH_2Cl_2 and the solvent interception products **177** and **178** in MeCN and THF, respectively (Scheme 71).

Scheme 71



Note that with all amides irrespective of substituents in the amide group, triphenyl(vinyl)silane **176** gave the same product of bromoamination **179**, thus proving that the reaction proceeded as interception of the solvent molecule (MeCN) rather than by the attack of the amide molecule (Scheme 72). Both compound **179** and the Ritter-type product **177** (see Scheme 71) were quantitatively cyclized to the corresponding oxazolines **180**, **181**.[123] The difference between amides and sulfonamides was explained by the low nucleophilicity of the nitrogen atom due to its conjugation with the carbonyl group, that made the oxygen atom the center of basicity, in contrast to the case of sulfonamides; as a result, heterocyclization occured on the amide oxygen

Scheme 72



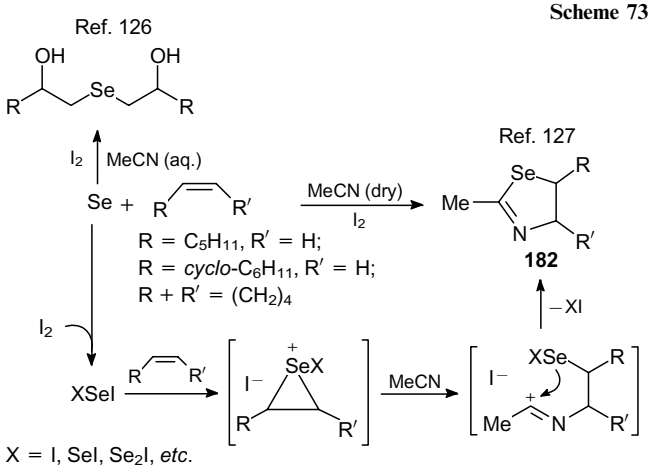
R′ = Me, Ph, CF_3; **180**: R = Ph, R′ = Me; **181**: R = Me, R′ = CF_3

rather than on the nitrogen atom (which would give *N*-acylaziridines).

4. Miscellaneous syntheses of N,heteroatom-containing heterocycles

Much less studied as compared to N-, N,O-, or N,S-heterocycles are 1,3-selenazoles and 1,3-selenazolines, whose synthesis includes several steps, or makes use of hardly accessible reagents as the source of selenium (see, *e.g.*, Ref. 124 and references cited therein). To the best of our knowledge, there is only one work in which elemental selenium was employed.[125] Recently, the iodine-assisted reaction of elemental selenium with alkenes in aqueous acetonitrile producing β-hydroxyselenides was reported.[126] Taking into account the aforementioned formation of the Ritter-type products of solvent interception, we found that the same reaction carried out in anhydrous acetonitrile represented a novel method for assembling 1,3-selenazoline skeleton from the simplest building blocks in one preparative step (Scheme 73).[127]

Scheme 73

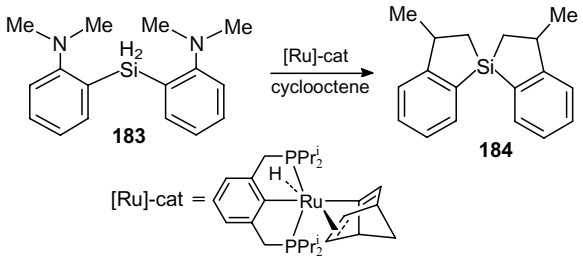


X = I, SeI, Se_2I, *etc.*

The shown mechanism nicely explained the observed difference between the reaction course in aqueous and anhydrous acetonitrile, since in MeCN – H_2O mixtures the nucleophilicity of water was increased due to the H-bonding with acetonitrile, whereas the nucleophilicity of anhydrous acetonitrile was much higher than in the presence of water.

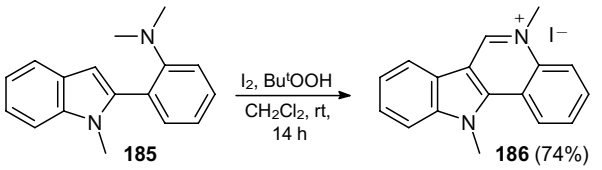
An unusual silicon-centered spirocycle **184** was synthesized recently by dehydrogenative intramolecular silylation of the C(sp^3) – H bonds of 2,2′-silanediylbis(*N*,*N*-dimethylaniline) **183** with Ru-phosphine catalyst and cyclooctene as a hydrogen acceptor (Scheme 74).[128]

Scheme 74



The highly promising biological activity of isocryptolepine, an indoloquinoline alkaloid, and its salts prompted Volvoikar and Tilve [129] to elaborate a new synthetic protocol based on oxidative cyclization of 2-(*o*-*N*,*N*-dimethylanilino)indole **185**. A small number of previous studies on the synthesis of polycyclic benzimidazoles was summarized in a review.[130] The highest yield (74%) of the salt product **186** was attained by carrying out the reaction in chloroform with iodine as a halogen source and Bu^tOOH as an oxidant (Scheme 75).

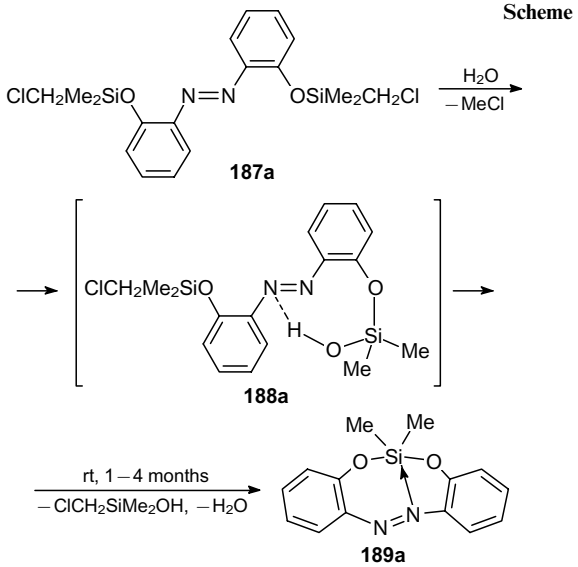
Scheme 75



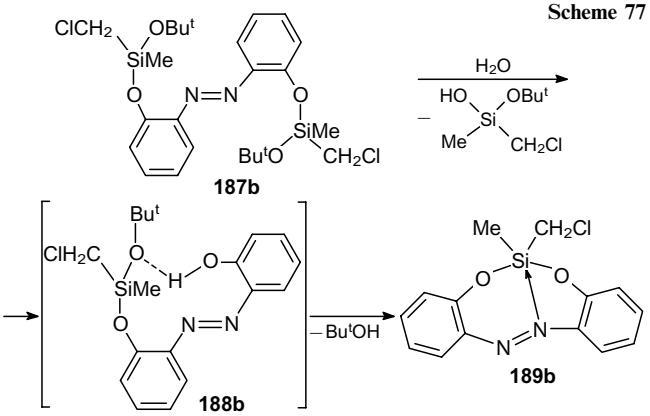
Recently, bis[(chloromethyl)diorganylsiloxy]azobenzenes **187a** have been synthesized and their hydrolysis accompanied by cyclization into cyclic silicon-containing diazenes **188a** with intramolecular N → Si bond was studied (Scheme 76).[131] The easy hydrolysis is due to the high oxophilicity of the silicon atom.

The replacement of a methyl group at the silicon atom by the *tert*-butoxy group changes the course of the reaction so that, upon prolonged storage at room temperature, as depicted in Scheme 76, bis(azobenzene) **187b** eliminates the molecule of Bu^tOH (Scheme 77).[131] The unexpected cleavage of the Si – OBu^t bond can be due to the hydrogen

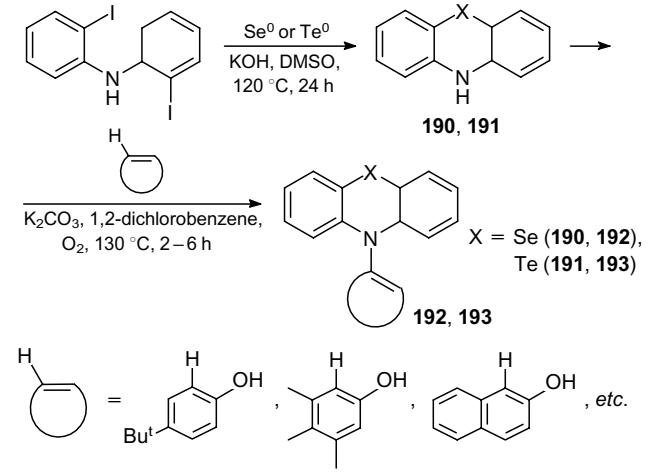
Scheme 76



Scheme 77



Scheme 78



bonding in the intermediate **188b**. The formation of the N → Si coordination bond in compound **189b** was confirmed by ^{29}Si NMR spectroscopy.

Cremer *et al.*[132] recently synthesized fused heavy chalcogen analogues of 10,10a-dihydro-4a*H*-phenoxazine and -phenothiazine **190**–**193** using elemental chalcogens *via* dehydrogenative C–H phenochalcogenazination (Scheme 78). Depending on the substituents in the aryl groups, the isolated yields varied from moderate (52%) to excellent (95%). The structure of one of the products was confirmed by X-ray diffraction analysis.

5. Conclusion

The review represents the latest results, mainly since 2015, on the synthetic approaches to various *N*-heterocycles based on intramolecular oxidative cyclization. The interest in these compounds and methods of their synthesis is due to their biological activity and the possibility of further transformations by introduction of biologically active moieties. Two main strategies are considered: dehydrogenative C–C, C–N, C–O, N–N, or N–S bond coupling accompanied by cyclization, and two-step oxidative amination followed by dehydrohalogenative cyclization. A variety of methods includes different metal-catalyzed or catalyst-free protocols, the use of various MW, UV, visible light-assisted syntheses, diverse oxidants [O_2, S, H_2O_2, I_2, Ce(IV), CuI, $FeCl_3$, $FeBr_3$, $KHSO_5$, $K_2S_2O_8$, ButOOH, ButOI, PhI=O, $PhI(OAc)_2$, NBS, NIS, TEMPO, Selectfluor™] and reaction conditions, allowing preparation of the target compounds in good yields and selectivity. A large family of the resulting heterocycles includes aziridines, pyrroles, diazoles, thiazoles, 1,2,4-triazoles, tetrazoles, 1,2,4- and 1,3,4-thiadiazoles, indazoles, benzodiazepines, quinazolines, selenazolines, and various mono- and polycyclic Si,N-heterocycles, some of which were obtained for the first time. I believe that the present review provides the reader with a guide to choosing the most suitable method for the synthesis of the required N-heterocycles.

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6. List of acronyms

Bn — benzyl,
Bs — besyl (benzenesulfonyl),
Fu — furyl,
HFIP — hexafluoroisopropanol,
LED — light emitting diode,
m-CPBA — *meta*-chloroperoxybenzoic acid,
Ms — mesyl (methanesulfonyl),
MW — microwave irradiation,
Ns — nosyl (*para*-nitrophenylsulfonyl),
NXS — N-halosuccinimide [X = I, *N*-iodosuccinimide (NIS), X = Br, *N*-bromosuccinimide (NBS],
PIDA — phenyliodine(III) diacetate,
PIFA — phenyliodine(III) bis(trifluorodiacetate),
SET — single electron transfer,
Tf — triflyl (trifluoromethanesulfonyl),
Th — thienyl,
Ts — tosyl (*para*-tolylsulfonyl).

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