Review

Ag-Mediated Reactions: Coupling and Heterocyclization Reactions

Jean-Marc Weibel, Aure#lien Blanc, and Patrick Pale

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Ag-Mediated Reactions: Coupling and Heterocyclization Reactions

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1. Introduction

Because of their d^{10} electronic configuration, coinage metals are at the borderline between main group elements and transition metals. Transition metals usually exhibit Lewis acid character, more or less pronounced depending on their position in the Mendeleev Periodic Table.

In the coinage metal series, silver and gold nevertheless exhibit special properties due to the availability of the f orbitals and relativistic contraction of their electron cloud (Figure 1). Both of them thus still present a marked Lewis acid character.[1–4]

The applications of silver salts, mainly Ag^I, in organic synthesis are indeed mostly driven by this Lewis acidity. However, in several applications, it seems that it is much more the (in)solubility properties of silver salts which actually are driving reactions. Indeed, in many reactions where halogens play a key role, silver salts often activate reactions by specifically interacting with the halogen atom and forming insoluble silver halides, the so-called halogenophilicity of silver. This "effect" has been widely used in organic synthesis, mainly in nucleophilic substitutions[5] (Scheme 1), including glycosylations[6] (Scheme 2), in some eliminations[7] (Scheme 3) and in processes involving organometallics (see section 2.2).

The d^{10} electronic configuration favored interactions of Ag^I with unsaturated systems having low-lying empty orbitals, especially alkynes, and to a lesser extent allenes and alkenes. This alkynophilicity is probably reinforced by f orbitals and relativistic effects.[2,3]

Nevertheless, silver salts are able to act either or both as σ-Lewis acid or π-Lewis acid. Interestingly, calculations reveal that σ-coordination of Ag^I is slightly preferred over π-coordination and that this preference is higher for nitrogen than for oxygen Lewis bases (Figure 2).[8]

From an organic point of view, this alkynophilicity, and π-coordination in general, have dramatic consequences on the behavior of alkynes and any π-system. Upon coordination, the π-system becomes prone to nucleophilic addition, and if a (hetero)nucleophile is included within the same molecule, the formation of (hetero)cycles is expected (Scheme 4, bottom line). If the starting unsaturated system is a terminal or a silylated alkyne, the behavior could be different since the silver π-complex could evolve toward the corresponding silver acetylide.[9] In this case, the so formed silver acetylide can react as a nucleophile, as any organometallics. It can thus be trapped by various electrophiles, such as deuterium, halogen, or silyl derivatives.[10] More interestingly, silver acetylides can be transmetalated and thus engaged in various reactions and especially cross-coupling reactions (Scheme 4, top).

In this review, we will thus focus on both aspects, that is, cross-coupling reactions involving silver salts and the formation of heterocycles promoted by silver salts.

2. Coupling Reactions Promoted by Silver Salts

2.1. Context

The term coupling encompasses a large variety of reactions where a new C−C bond is created, usually through a formal nucleophilic substitution.[11] For such reactions, metal-catalyzed versions have been developed and rapidly have become one of the most important tools in organic synthesis.[12]

Among the metals already employed for such reactions, palladium has amply proven to be the most versatile, its salts or complexes catalyzing connection between alkyl, alkenyl, or alkynyl groups.[13–16] In this context, the coinage metals offer unique properties and among them, silver exhibits

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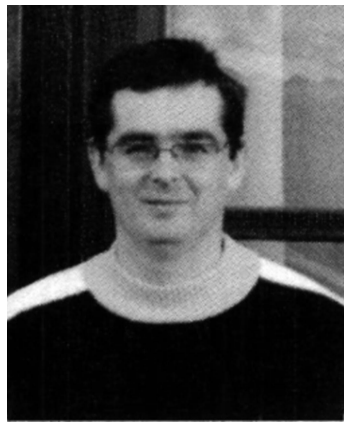

J.-M. Weibel obtained his Ph.D. in chemistry in 1994 from the Université Louis Pasteur of Strasbourg under the supervision of Dr. D. Heissler. After a two years' stay at University College of London as a postdoctoral fellow with Prof. W. B. Motherwell, he joined Prof. Pale's group at the Chemistry Institute of Strasbourg in 1996 as assistant professor. His research interests focused on the development of new tools for the organic chemist and on their application in total synthesis of molecules with biological activities.

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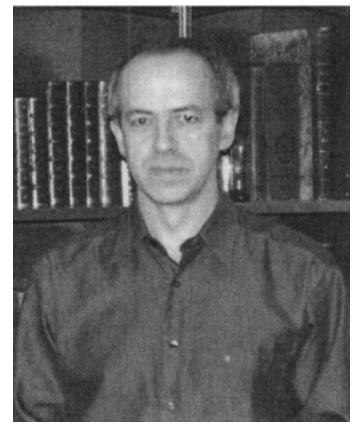
typical behaviors, so that silver salts have increasingly gained interest as catalyst or cocatalyst in various cross-coupling reactions. In these reactions, silver salts have been applied for two main reasons:

(i) They can abstract halides from organometallic intermediates, rendering the metal (Pd) more electropositive and opening a vacant site in the coordination sphere. In these cases, the main role is thus to form insoluble silver halides while activating the actual catalytic species.

(ii) They can produce organosilver species, which can either react as such or more often be transmetalated to various metals or organometallics, especially organopalladium intermediates.

Both aspects will be examined in this section, with a special emphasis on the second since the use of silver salts



P. Pale studied at the University of Champagne-Ardenne, France, where he obtained a Ph.D. in 1982 under the direction of Prof. J. P. Pete and J. Muzart. After an industrial stay in a pharmaceutical company, he joined the group of Prof. L. Ghosez at Louvain-La-Neuve in Belgium for postdoctoral work on the development of azadienes. In 1984, he returned to the University of Champagne-Ardenne as a CNRS fellow. Working on rearrangements and reaction mechanisms, he obtained a "Doctorat d'Etat" (Habilitation) in 1988, and then a research associate position at Harvard University in the group of Prof. G. Whitesides from 1988 to 1990. He returned to the University of Champagne-Ardenne, and took up his position in 1995 as Professor of Organic Chemistry at the Université Louis Pasteur in Strasbourg. Subsequently, he was awarded Professor at the Institut Universitaire de France from 1996 to 2001. His scientific interests include total synthesis of bioactive compounds, organometallic chemistry, asymmetric synthesis, carbohydrate chemistry, and enzymatic chemistry.

to abstract halogen is so common in cross-coupling reactions, and especially in Pd-catalyzed reactions, that it is beyond the scope of this review, and only a few typical examples will be reported here.

2.2. Coupling Reactions Driven by Silver Halide Formation

The role of silver salts as halogen abstracter has been demonstrated in various stoichiometric reactions, including those involving palladium complexes in connection with the formation of C−C bond. One of the earliest examples was the vinylation of benzene promoted by silver acetate with vinylpalladium(II) complexes.[17] In this reaction, silver acetate abstracted chloride from the vinylpalladium species, making the coordination of benzene possible. The resulting intermediate complex led to vinylbenzene formation after reductive elimination (Scheme 5).

Silver perchlorate has been used to promote the regioselective insertion of a diene into the Pd−C bond of a (η^1-aryl)palladium bromide complex, as well as its isomerization to an (η^3-allyl)palladium complex (Scheme 6). This process occurred through the intermediate formation of an (η^1-η^2-enyl)palladium species from the starting (η^1-aryl)palladium bromide complex.[18]

In catalyzed reactions, halide abstraction by silver ion also occurred and sometimes altered the overall reaction pathway, as in some Heck reactions. Heck reactions are widely used in organic synthesis, from natural product total synthesis to industrial processes, and allow the construction of C−C bonds between aryl or alkenyl groups and alkenyl motifs.[12,15,16] In these reactions, a base is required to trap the acid liberated (Scheme 7).

Addition of silver salts in Heck reactions facilitated and improved such reactions. Addition of silver salts having

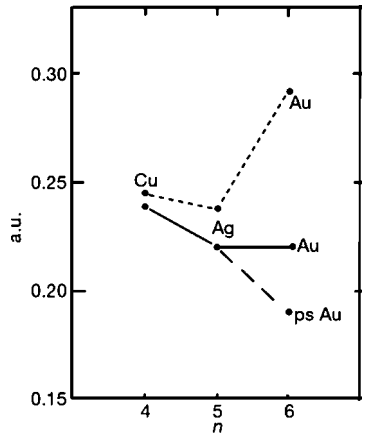
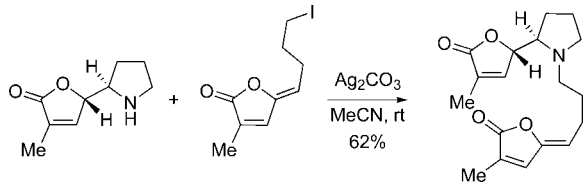
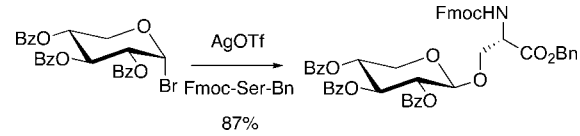


Figure 1. Calculated ionization potentials for the Group 11 transition metals using three different methods: relativistic Dirac-Hartree-Fock (full line), non-relativistic Hartree-Fock (dashed line), and pseudopotential without the lanthanide contraction (large dashed line). The experimental ionization potentials closely match those given by DHF. (Reprinted with permission from ref 1. Copyright 1975 Elsevier).

Scheme 1



Scheme 2



Scheme 3

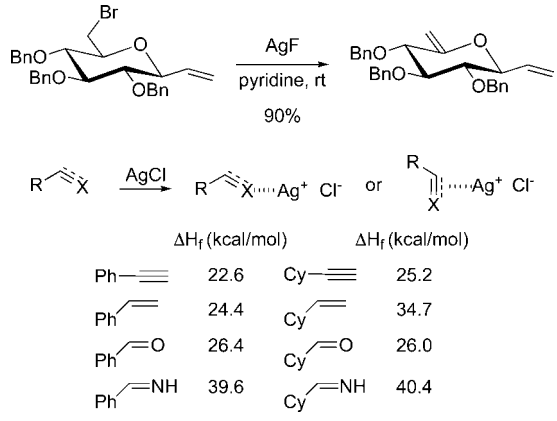
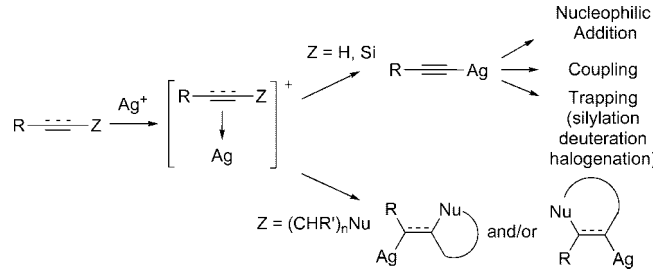


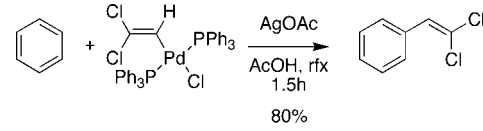
Figure 2. Computed heats of formation (B3LYP/SDD, kcal mol^{-1}) of various substrates with AgCl (Reprinted with permission from ref 8. Copyright 2007 American Chemical Society).

poorly nucleophilic counterions usually increased the reaction rates, especially when aryl or alkenyl halides are used as starting materials. In these cases, Ag^+ abstracted the halide from the Pd^{II} complex generated by oxidative addition of the aryl or alkenyl halide to Pd^0.[19–21] This step produced a cationic Pd^{II} complex if a non-nucleophilic Ag counterion was selected (Scheme 8). This cationic Pd^{II} complex thus bound more efficiently to the alkene than

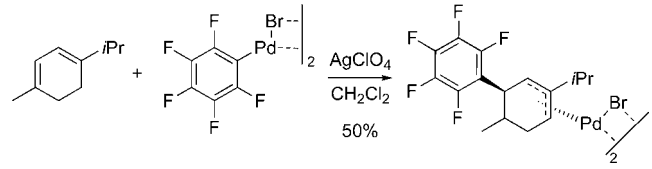
Scheme 4



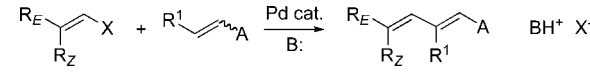
Scheme 5



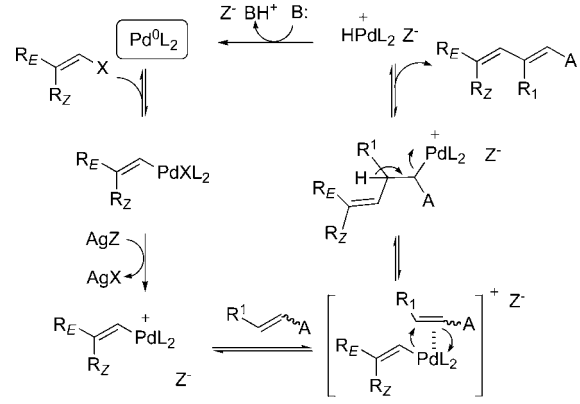
Scheme 6



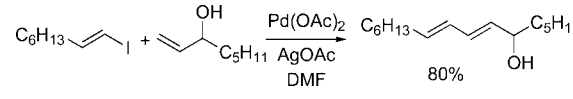
Scheme 7



Scheme 8



Scheme 9

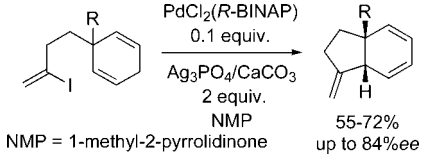


the corresponding halogenated Pd^{II} complex. Insertion to the alkene then produced an alkyl Pd^{II} complex, which suffered from β-elimination. The latter step produced a hydridopalladium species, which regenerated the active Pd^0 catalyst upon treatment with base. This step must be fast enough to avoid the liberation of proton or the readdition of the hydridopalladium species, processes known to be responsible for alkene isomerization, a frequent problem in Heck reactions.[22]

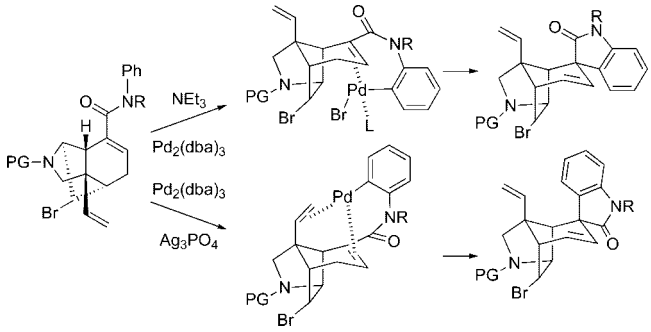
Silver nitrate, acetate, carbonate, and triflate are thus common additives in Heck reactions (Scheme 9).[23]

Combining both aspects with its basic counterion, silver phosphate is among the best additives. With such additives,

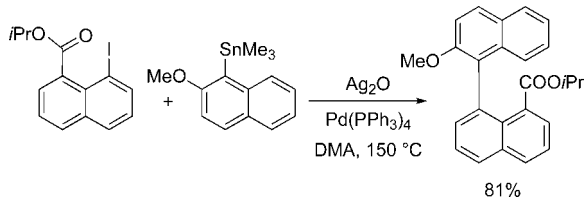
Scheme 10



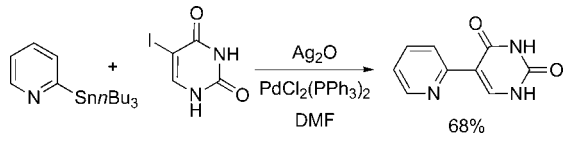
Scheme 11



Scheme 12



Scheme 13



high diastereo- and enantioselectivities can be achieved (Scheme 10).[24–26]

Moreover, the reaction course and thus the products could be different, since the Ag-promoted formation of a less coordinated palladium species led to any possible complexes with this Pd species. This property has been exploited in alkaloid synthesis (Scheme 11).[27]

Stille reactions are also improved in the presence of silver salts, and here also numerous examples, beyond the scope of this review, have been reported.[12,15,16]

For example, addition of silver oxide allowed producing hindered 1,2-substituted binaphtyl derivatives in high yields (Scheme 12).[28]

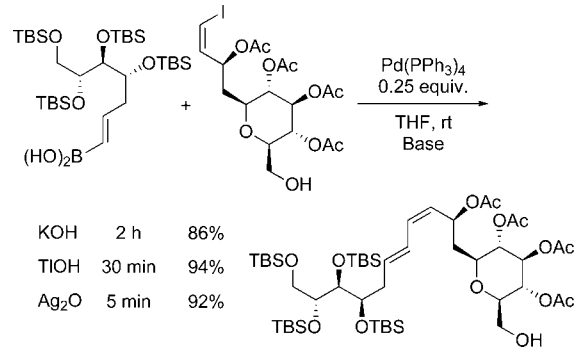
In similar conditions, 5-iodouracil could be coupled with stannylated pyridine, forming 5-(2-pyridinyl)uracil in good yield (Scheme 13).[29]

In parallel, silver oxide was also used as activator in various Suzuki coupling reactions. The earliest example could be traced back to Kishi's palytoxin synthesis. Silver oxide, as well as thallium hydroxide, provided dramatic rate enhancements of some vinylboronic acids couplings (Scheme 14).[30]

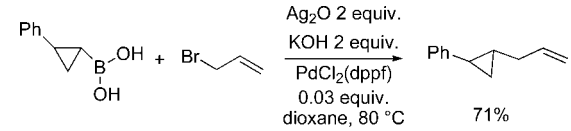
More recently, silver oxide was used as activator for the Pd-catalyzed coupling of cyclopropylboronic acids to allyl bromides (Scheme 15).[31]

Cyclopropanes themselves could be obtained through an interesting coupling-cyclization reaction promoted by

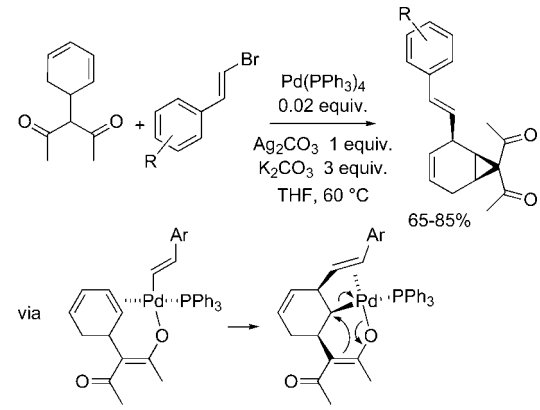
Scheme 14



Scheme 15



Scheme 16



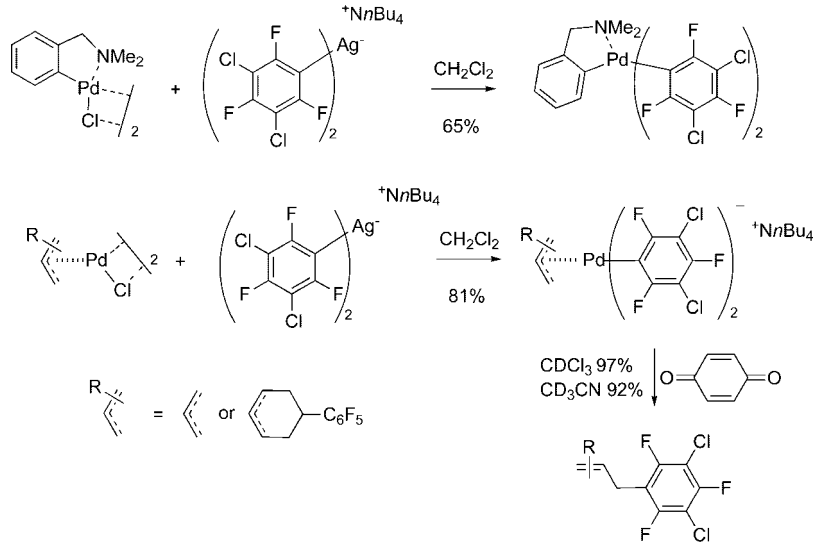
palladium and silver salts. In the presence of palladium tetrakis(triphenylphosphane) as catalyst with a stoichiometric amount of silver carbonate and potassium carbonate in refluxing THF, β-bromostyrenes added across dienes carrying a β-diketosubstituent and further evolution lead to cyclopropyl styryl alkenes, usually in good to high yields (Scheme 16). Interestingly, the styryl and cyclopropyl groups in the product exhibited a *syn* stereochemistry, revealing some insights into the mechanism of this reaction.[32]

2.3. Coupling Reactions from Organosilver Species

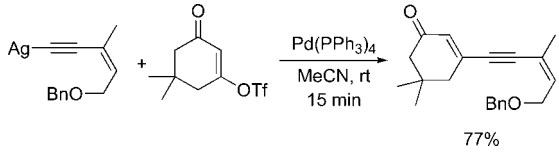
Preformed organosilver species can be directly used as a reagent for the formation of C−C bonds or as a precursor in various cross-coupling reactions via transmetalation. In these cases, a stoichiometric amount of organosilver was required. However, only very few stoichiometric reactions involving organosilver species are known, and they usually are involved in mechanistic studies.

Arylargentates can be transmetalated either to (η^1-aryl)palladium complexes or to (η^3-allyl)palladium complexes (Scheme 17). Upon addition of benzoquinone, reductive elimination occurred and the aryl group was transferred to the allyl system, providing allylbenzene derivatives.[33,34]

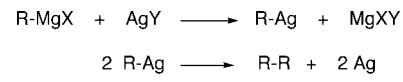
Scheme 17



Scheme 18



Scheme 19



Alkynyl silvers, easily produced either from the corresponding alkynes[35] or from silylated alkynes,[36] are stable reagents, and nevertheless, they can react with vinyl triflates or aryl iodides in palladium-catalyzed cross-coupling reactions.[37] This reaction is best catalyzed by palladium tetrakis(triphenylphosphine). In this reaction, alkynyl silvers are clearly transmetalated to the vinyl or aryl palladium species formed by oxidative insertion of the zerovalent palladium species into organic halide or triflate (Scheme 18).

2.4. Coupling Reactions Driven by in Situ Organosilver Formation

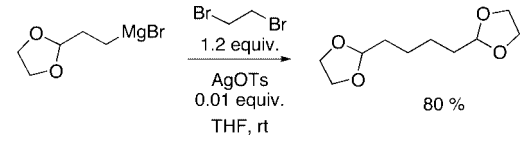
2.4.1. Ag-Catalyzed Homocoupling Reactions

The earliest coupling reactions involving silver salts could be traced back to the studies of Wurtz-type coupling of Grignard reagents in the presence of various metal salts.[38–40] These studies revealed that silver salts catalyzed alkyl−alkyl homocoupling of Grignard reagents, and that they do so by transmetalation and then recombination (Scheme 19).

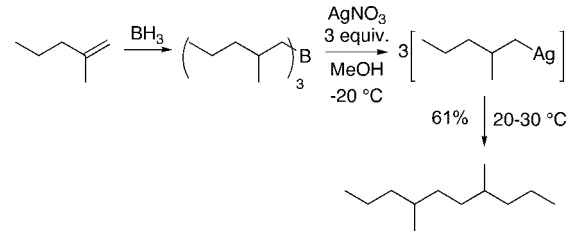
This homocoupling was applied to Grignard reagents derived from 2- or 4-bromopyridine and patented for producing 2,2′- or 4,4′-bipyridines.[41] More recently, the same reaction was slightly modified using silver tosylate as catalyst (1 mol %) and 1,2-dibromoethane as reoxidant (Scheme 20).[42]

In related studies, Brown et al. showed that alkylboranes, obtained from hydroboration of the corresponding alkenes, could be transmetalated to silver salts provided that hydroxide was added. The so-formed alkyl silver seemed to be stable at low temperature, but placed at room temperature, they

Scheme 20



Scheme 21



evolved as described above and gave the homocoupling product (Scheme 21).[43–45]

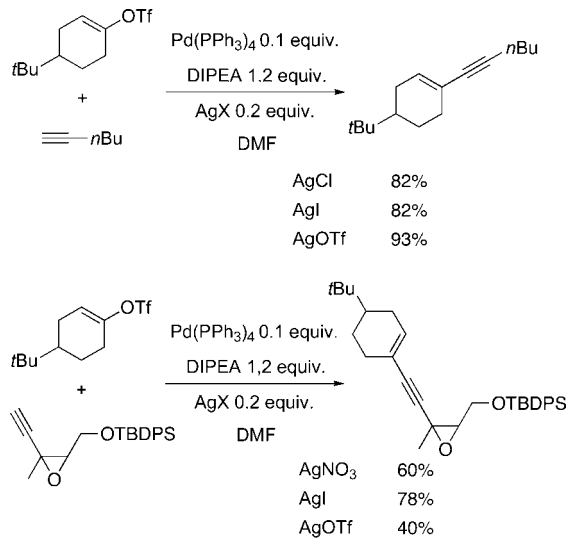
2.4.2. Pd−Ag-Catalyzed Coupling Reactions

The use of silver salts in cross-coupling reactions is mainly related to the synthesis of enynes.[46] And indeed, one of the earliest contributions in this area is related to solving synthetic problems. For the synthesis of antitumoral dienediynes, the Pale's group developed mild sp-sp^2 cross-coupling reactions, catalyzed by a new combination of catalysts: $Pd(PPh_3)_4$ and silver salts.[47–49] In this case, Sonogashira, Linstrumelle as well as Cacchi's conditions proved to be noncompatible with such syntheses and especially with the use of alkynyloxiranes as reagents in such coupling reactions. In sharp contrast, silver salts and especially silver halides were very effective as cocatalysts, cleanly providing the expected coupling products, even with the sensitive alkynyloxiranes (Scheme 22). Interestingly enough, this combination of catalysts avoided the formation of homocoupling products, common side-products resulting from Glaser-type reaction when using Cu^I-catalysts.[50–52]

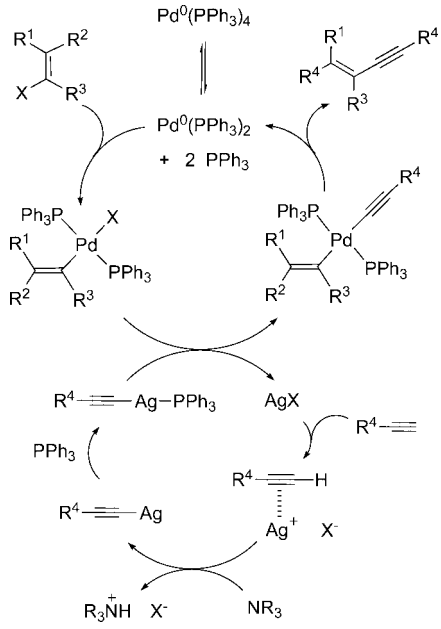
A systematic study revealed that silver iodide in DMF was the best catalyst for sensitive compounds, although other silver salts and a variety of solvents like benzene, chloroform, etc. could be used (Scheme 22).[9,53]

More recently, the mechanism of this Pd−Ag-catalyzed coupling was investigated mainly through ^{109}Ag NMR and

Scheme 22



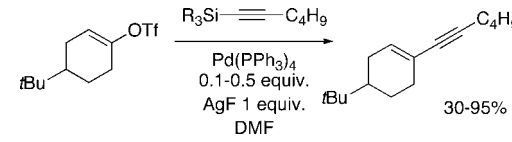
Scheme 23



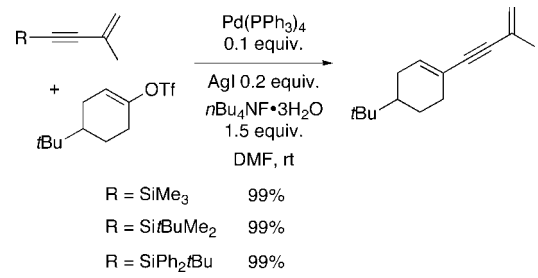
ESI-MS techniques (Scheme 23).[9] The alkyne was first coordinated by the silver salt, as revealed by significant shifts of the acetylenic and propargylic protons and carbons, as well as ^{109}Ag in the corresponding NMR spectra. This π-complex was also detected by ESI-MS. π-Coordination rendered the acetylenic C−H bond more fragile and, upon addition of base, the acetylenic proton was abstracted. This step was clearly very rapid since only the resulting alkynyl silver was then detected. Such species are usually poorly soluble as such due to their polymeric structures. However, in the Pd−Ag-catalyzed coupling reaction, the palladium source ($Pd(PPh_3)_4$) was far from innocent and the triphenylphosphine liberated by decoordination from this source coordinated the alkynyl silver, stabilizing and rendering it more soluble.[54] The alkynyl silver then entered in the palladium catalytic cycle at the transmetalation step as demonstrated earlier (see section 2.3).[37]

In order to solve regioselectivity problems in total synthesis of polyenynes, Pale et al. modified their Pd−Ag catalytic conditions to achieve cross-coupling of any 1-trialkylsilyl-1-alkyne with aryl or vinyl iodides or triflates, without prior

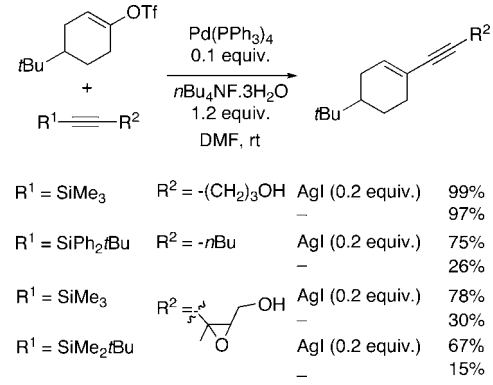
Scheme 24



Scheme 25



Scheme 26



deprotection.[55,56] For mechanistic reasons, preliminary investigations were based on AgF as promoter, with the hypothesis that 1-trialkylsilyl-1-alkyne would be converted into silver acetylide with this catalyst (Scheme 24).[57]

Eventually, trimethylsilyl-, *tert*-butyldimethylsilyl-, *tert*-butyldiphenylsilyl-, or triisopropylsilyl alkynes were easily coupled at room temperature with various iodides or triflates in the presence of catalytic amounts of $Pd(PPh_3)_4$ and silver salt and stoichiometric amount of tetrabutylammonium fluoride trihydrate (Scheme 25).[56]

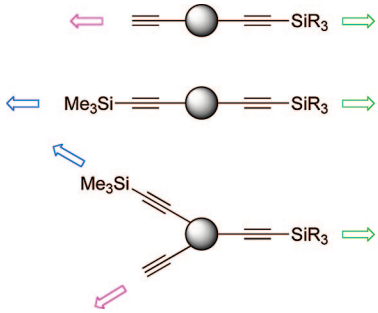
It is worth noting that during this study it was found that tetrabutylammonium fluoride trihydrate alone was able to promote the same coupling in the presence of catalytic amounts of $Pd(PPh_3)_4$, but under these conditions, the reaction rate was clearly dependent on the bulkiness at the silyl atom and on the substrate structure (Scheme 26).[57]

To go further into the chemoselectivity of cross-coupling reactions and with synthetic applications in mind, especially toward organic materials (Scheme 27), the same group also tried and succeeded in setting up conditions which are able to distinguish between alkynes protected with various silyl groups.[58]

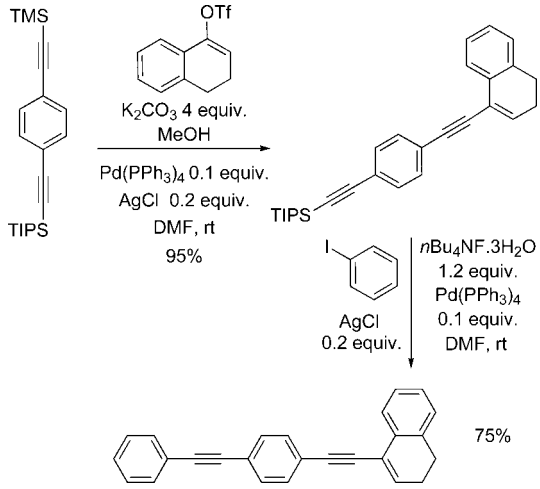
Indeed, 1-trimethylsilyl-1-alkynes were selectively coupled in the presence of other silylated acetylenic moieties using $Pd(PPh_3)_4$-AgCl as catalysts together with 4 equiv of methanol and potassium carbonate in DMF at room temperature.[59] Combined with the preceding conditions, this method allowed for successive coupling reactions, each one being selective of a silylated alkyne (Scheme 28).[58]

This set of Pd−Ag catalyzed reactions culminated with the successive couplings of a triyne, its acetylene moieties

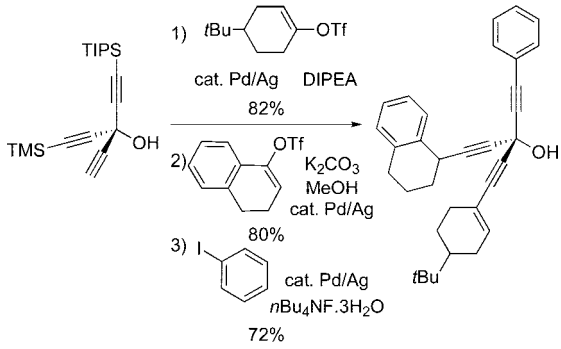
Scheme 27



Scheme 28



Scheme 29



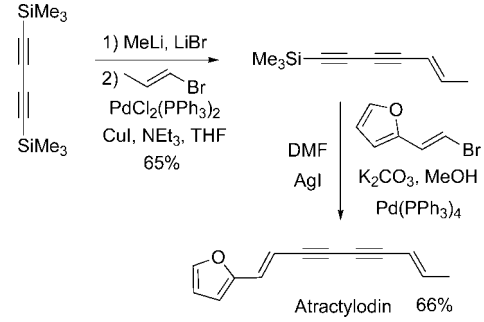
being respectively nonsubstituted, trimethylsilyl substituted, and triisopropylsilyl substituted (Scheme 29). Interestingly enough, since these coupling reactions required the same Pd and Ag-catalysts, a one-pot process was performed, in which each coupling partner and the appropriate activating agent are successively added.[58]

An interesting development of these coupling reactions afforded an alternative strategy toward conjugated diyne compounds and especially natural polyacetylenic products. Instead of the classical Cadiot-Chodkiewicz synthesis, substituted conjugated diynes could now be obtained through sequential coupling of 1,4-bis silylated butadiyne (Scheme 30).[60,61]

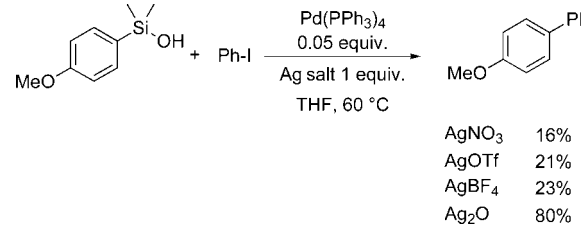
Silver oxide proved to be also a good promoter of cross-coupling reactions between aryl iodides and various sp- or sp^2-carbon species.

Originally discovered with aryl silanols along Hiyama's systematic work dealing with the transformation of C−Si to C−C bond, this coupling reaction required palladium tetrakis(triphenylphosphane) as catalyst but a stoichiometric amount of silver oxide as well as heating (Scheme 31).[62]

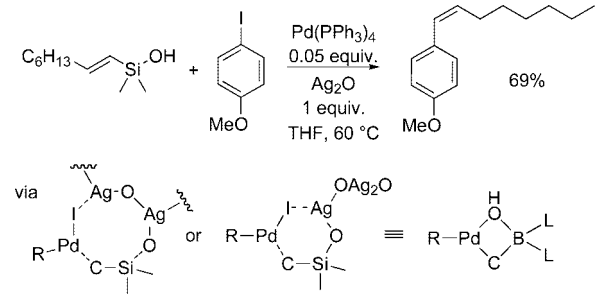
Scheme 30



Scheme 31



Scheme 32

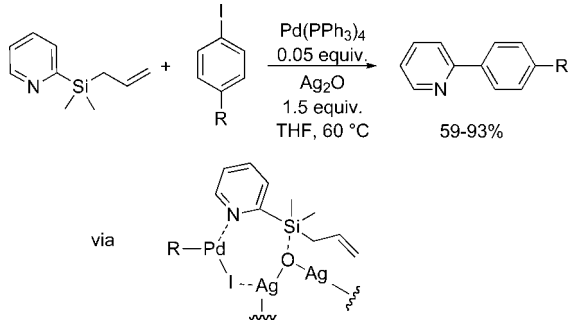


Interestingly, these conditions allowed coupling vinylsilanols in good yields (Scheme 32). The corresponding aryl or vinyl silanediols or triols could also be coupled, but not silyloxysilanes, revealing the key role of the free hydroxyl group at the silicon center.[63] Polyalkenylsiloxanes could also serve as a partner in the cross-coupling reaction using these conditions.[64] However, this coupling reaction seemed limited to aryl iodides since bromides and more surprisingly triflates did not react under these conditions.[62,63] These limitations could be rationalized by the involvement of transmetalation intermediates in analogy to those described for Suzuki couplings (Scheme 32).[65–67]

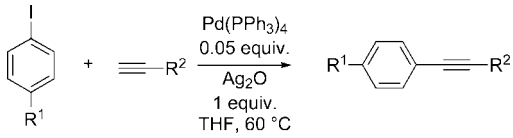
Interestingly, 2-pyridinylallylsilanes reacted in similar conditions and transferred the pyridine moiety to various aryl iodides (Scheme 33).[68] It is worth noting that 3-pyridinylallylsilanes did not react under these conditions, revealing the key role played by pyridine nitrogen and a cyclic transmetalation intermediate similar to those mentioned above could thus be envisaged.[67]

The same conditions, palladium tetrakis(triphenylphosphane) as catalyst with a stoichiometric amount of silver oxide in refluxing THF, proved to be also efficient for the coupling of terminal alkynes. It is worth noting that in this case, silylated alkynes did not undergo coupling (Scheme 34). As for aryl or vinylsilanols, this coupling seemed limited to aryl iodides; bromides and more surprisingly triflates did not react under these conditions.[69,70]

Scheme 33

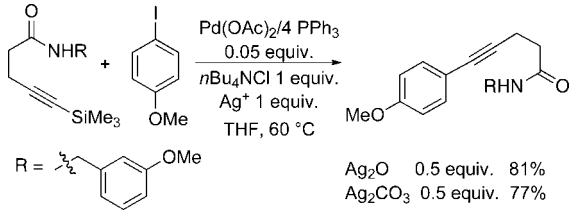


Scheme 34



R^1 = H, R^2 = $SiMe_3$	79%
R^1 = OMe, R^2 = $SiMe_3$	60%
R^1 = COMe, R^2 = $SiMe_3$	99%
R^1 = COMe, R^2 = *t*Bu	87%
R^1 = H, R^2 = Ph	60%

Scheme 35



In sharp contrast, Nagasaka et al. reported that 1-trimethylsilyl-1-alkynes could be coupled with aryl iodides in the presence of silver carbonate or silver oxide in the presence of palladium catalyst and tetrabutylammonium chloride. In this coupling reaction, as in the preceding one, a stoichiometric amount of silver ion was required and only iodides but not bromides or triflates were effective as a coupling partner (Scheme 35).[71]

Jeong et al. also applied the same conditions to coupling reactions of bis(trimethylsilyl)enediynes and afforded bis(aryl)enediynes.[72]

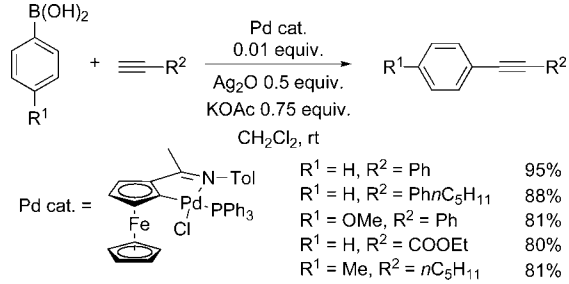
Interestingly, a recent report broadened the scope of such couplings. Wu et al. showed that aryl boronic acids as well as boronates could be engaged in coupling reactions with terminal alkynes in the presence of a palladacycle as catalyst and silver oxide. Here again, the amount of silver ion was critical for the reaction efficiency. Stoichiometric amount of Ag^+ was indeed required to obtain high yields (Scheme 36), while lower amounts dramatically reduced yields (e.g., 50% yield at 10 mol % Ag_2O loading) and favored homocoupling byproduct.[73]

Recently, Mori et al. reported conditions based on Pd and AgF or $AgNO_3$/KF enabling the coupling of heterocycles with aryl iodides (Scheme 37).[74–76]

2.4.3. Ag-Catalyzed Coupling Reactions

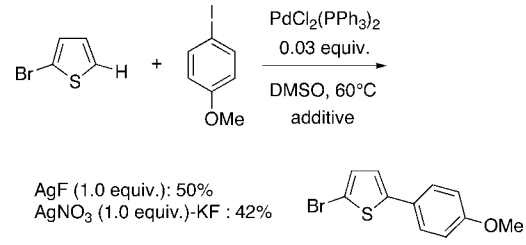
The coupling of terminal alkynes with aryl iodides or bromides could also now be performed without palladium but with silver as the sole catalyst. Recently disclosed by

Scheme 36

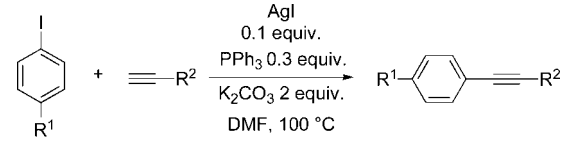


R^1 = H, R^2 = Ph	95%
R^1 = H, R^2 = PhnC_5H_{11}	88%
R^1 = OMe, R^2 = Ph	81%
R^1 = H, R^2 = COOEt	80%
R^1 = Me, R^2 = nC_5H_{11}	81%

Scheme 37



Scheme 38



R^1 = H, R^2 = Ph	95%
R^1 = NO_2, R^2 = Ph	99%
R^1 = OMe, R^2 = Ph	92%
R^1 = H, R^2 = Ph*p*Me	96%
R^1 = H, R^2 = Ph*p*F	98%
R^1 = H, R^2 = nC_6H_{13}	83%

Wang and Li, this reaction required a base and a ligand and proceeded best in polar solvents but at high temperature. Silver iodide together with triphenylphosphane proved to be the best catalyst combination, although other silver salts and phosphanes were also efficient. Potassium carbonate was the base giving the highest yield. Under these conditions, aryl iodides and aryl and alkyl acetylenes were coupled, regardless of their electronic character, giving the corresponding diarylacetylenes in good to excellent yields (Scheme 38).[77] These reaction conditions suggested the intermediate formation of alkynyl silver.[9,54]

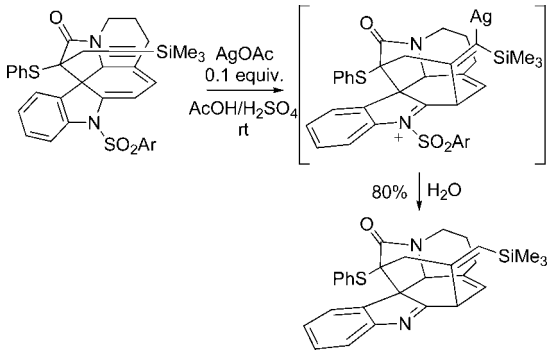
Silver salts have mainly been used for the synthesis of enynes or arylacetylenes through C−C bond formations, but a few other C−C bond formations have also been described.

Highly nucleophilic carbon entities such as enamines or enols could directly add to acetylenic or even ethylenic derivatives upon silver activation, in a process similar to the Conia reaction.[78–80]

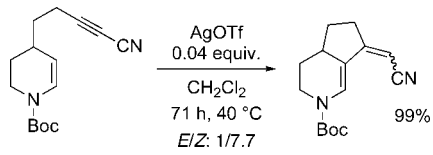
Intramolecular addition of enamines to some alkynes occurred in the presence of silver salt. One of the first examples of such a reaction was linked to the elaboration of the carbon skeleton of complex alkaloids from indoles (Scheme 39). The *N*-sulfonylated dienylamine derived from indole reacted as enamine toward a trimethylsilylacetylene moiety, probably activated by silver ion through π-complexation. A new six-membered ring was thus created.[81]

More recently, a similar process was described in which *N*-sulfonyl and *N*-Boc enamines added to tethered propiolate derivatives in the presence of silver triflate, leading to a mixture of diene derivatives (Scheme 40).[82]

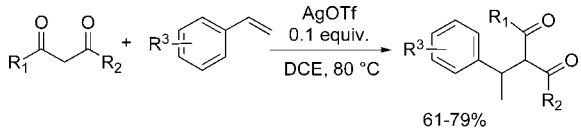
Scheme 39



Scheme 40



Scheme 41



In related but reversible reactions, enols derived from β-diketones proved to be able to attack styrenes and formed new C−C bond (Scheme 41).[83]

3. Heterocyclization Reactions Promoted by Silver Salts

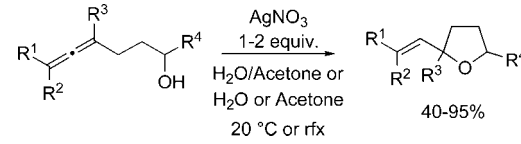
3.1. Context

Intermolecular addition of various nucleophiles to unsaturated substrates (alkynes, allenes, and alkenes) is a common process, known since the end of the XIX^{e} century. At that time, such a process was promoted by Brønsted acids, but in the search for less drastic and more selective conditions, it was found that mercuric salts were able to promote such nucleophilic additions to π-C−C bonds. However, Hg^{II} could be used as a catalyst or as a stoichiometric reagent, depending on the substrate structure. Later, it was also discovered that Pd^{II} salts in catalytic amounts are also effective for such transformations, leading to the industrial Wacker process.

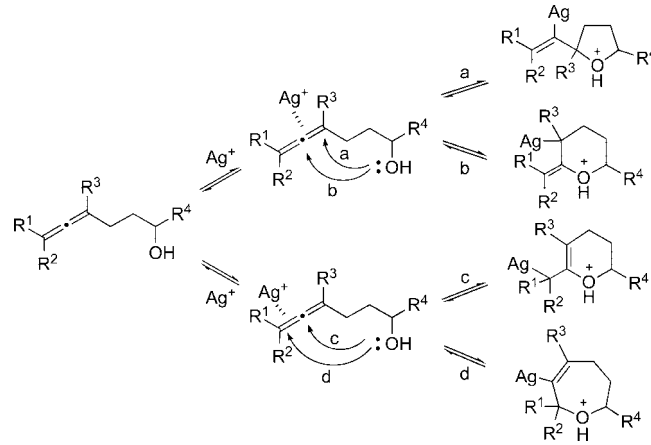
Despite their toxicity, mercuric salts were used for more than 70 years, leading to many applications to intermolecular and intramolecular additions of various nucleophiles to unsaturated C−C bonds. It is only at the end of the 70s that several other catalysts, including silver salts, were found. Serendipity seems to be at the heart of the discovery of silver salts as such catalysts. Indeed, Claesson and Goré independently reported that, in order to separate allenic alcohols or amines from their acetylenic progenitors, they treated these mixtures by silver nitrate and other salts and observed the formation of heterocycles instead of the expected separation.[84–86]

Heterocyclization reactions exhibit high interest in organic synthesis, especially when starting from alkynes or allenes since the cyclization products retain an olefin which can be further manipulated, opening a wide variety and diversity of applications. Moreover, the nature of the cyclization products can be varied by changing silver counterion and/or reaction conditions, and many intramolecular heterocyclizations proceed with high diastereoselectivity. These aspects will be developed in this section.

Scheme 42



Scheme 43



An extensive survey of the literature did not show examples of Ag-catalyzed formation of heterocycles implying heteroatom other than oxygen or nitrogen. Sulfur and selenium are probably too strong of ligands compared to unsaturated C−C bonds and they thus cannot be free in the presence of silver ion to add onto a silver coordinated π-bond.

3.2. Heterocyclization through C−O Bond Formation

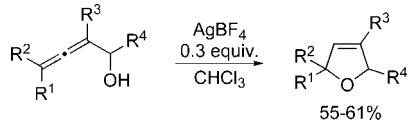
3.2.1. With Allenes

3.2.1.1. Cyclization of Allenols. As mentioned above, the cyclization of allenic alcohols was among the first examples of Ag-catalyzed heterocyclization. Indeed, while trying to isolate and separate a mixture of isomeric alkynyl and allenic alcohols with ammoniacal silver nitrate, Goré and Balme observed the quantitative formation of cyclization products (dihydropyrans).[86]

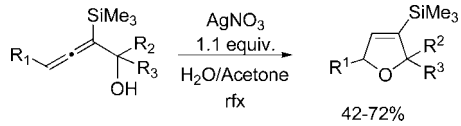
Exploring this reaction, the Goré's group showed that, in the presence of silver nitrate, γ-allenic alcohols were indeed efficiently converted into tetrahydrofurans bearing a vinyl group at the position adjacent to the oxygen atom (Scheme 42). This reaction can be performed either in acetone or in a mixture of acetone and water, or even in pure water; this reaction is thus an interesting and pioneering example of an ecofriendly reaction. It is worth noting that when the allene is di- or trisubstituted, only the *E*-vinyl oxolane is produced.[85,87]

The mechanism clearly involved the coordination of the double bond closer to the hydroxyl group and then an intramolecular addition of the hydroxyl group to this π-complex (Scheme 43). Among the four possible cyclization pathways, only the route leading to the shortest cycle (route *a* in Scheme 43) is operating whatever the substitution, in agreement with Baldwin rules.[88]

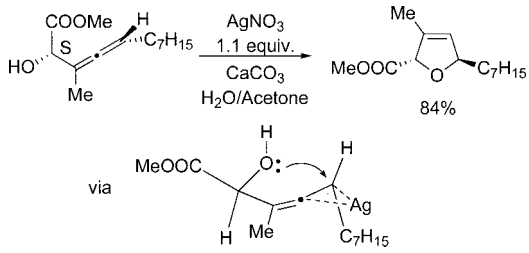
Scheme 44



Scheme 45



Scheme 46



In parallel, Claesson and Olsson, the progenitors of silver-catalyzed *N*-heterocyclization (see section 3.3), found that silver tetrafluoroborate in chloroform was the catalyst of choice for the ring closure of α-allenic alcohols (Scheme 44).[87]

From a mechanistic point of view, and as expected from Baldwin rules[88] with such a short chain between the allenic and hydroxy reactive parts, it is no longer the internal double bond of the allenic system, which is activated by Ag-coordination but the terminal one. The cyclization is no longer following an *exo*-trig pathway but an *endo*-trig pathway, leading to the formation of 2,5-dihydrofurans (Scheme 45).

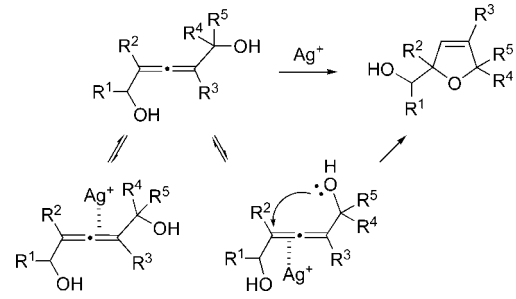
Trimethylsilyl-substituted α-allenic alcohols could also be converted to the corresponding 3-trimethylsilyl-2,5-dihydrofurans.[89] In this case, the conditions employed by Goré et al.[85,86] were used (Scheme 45). Secondary or tertiary alcohols seem to be required to get reasonable yields, while the presence of the silyl group on the allenic moiety is clearly not essential as revealed by related examples.

An interesting chiral and stereospecific version was proposed by Marshall et al.[90] With a stereodefined allene, the chirality at the hydroxyl group was preserved and thus induced the stereospecific formation of a *trans*- or *cis*-2,5-dihydrofuran: the *S* stereochemistry at the hydroxylated carbon gave the *trans* isomer, while the *R* gave the *cis* (Scheme 46). The role of the allene chirality was examined later, with the cyclization of chiral tetrasubstituted allenic alcohols revealing the preservation of the allene chiral information.[91]

The related cyclization of α-allenic diols exhibited surprising and remarkable preferences. Indeed, it has been shown that when these diols were dissymmetric, the more substituted one preferentially cyclized (Scheme 47).[92] This preference for cyclization of tertiary over secondary and over primary hydroxyl group seemed to be related to the formation of the less crowded π-Ag-complex, which thus induced the 5-*endo*-trig cyclization.

With a longer chain between the hydroxyl group and the allenic moiety, the Ag-catalyzed cyclization was still effective as shown by the Goré's group. Interestingly, β-allenic

Scheme 47



alcohols exclusively gave dihydropyrans, revealing that the terminal double bond of the allene was activated in this case, while δ-allenic alcohols gave tetrahydropyrans through activation of the proximal allenic double bond (Scheme 48).[93,94]

In a related work, Gallagher exquisitely exploited the probable transition state chair conformation of substituted δ-allenic alcohols to assess a highly diastereoselective synthesis of *cis*-2,6-disubstituted tetrahydropyrans (Scheme 49).[95]

On these bases, the Goré's group proposed an elegant synthesis of perhydrofurofurans or perhydrofuropyrans from allenic diols.[96] Depending on the chain length between the hydroxyl group and the allenic moiety, one or the other bicyclic ketal was obtained as single *cis* diastereoisomers (Scheme 50). However, the corresponding dihydropyrans were also produced, indicating that coordination and thus cyclization also occurred on the other (terminal) double bond for such allenes.

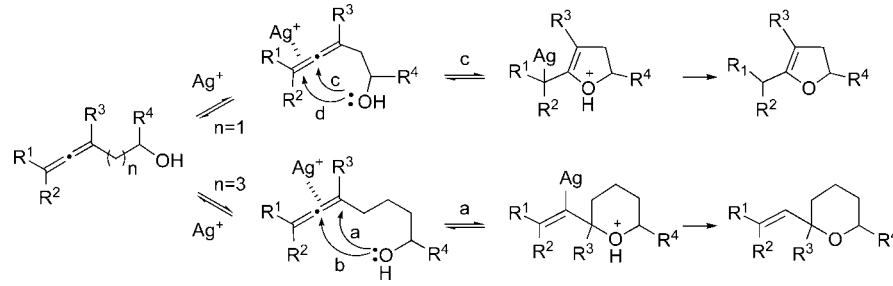
Seven-membered rings can also be obtained, as demonstrated by Grimaldi and Cormons, although in peculiar cases.[97] Indeed, these authors described the cyclization of β-allenic oximes to dihydro-4,7-oxazepines in good yields in the presence of silver tetrafluoroborate (Scheme 51). In this reaction, the hydroxyl of the oxime group attacked again the terminal double bond of the allenic system upon silver activation in a 7-endotrig process. This cyclization is in sharp contrast with a concomitant report (see section 3.3.1.2) describing the formation of nitrones from γ-allenic oximes.[173] This *N*- vs *O*-cyclization could be ascribed either to chain length differences between the oxime group and the allenic moiety or to the gem-dimethyl substitution in the Grimaldi-Cormons examples.

The Ag-mediated cyclization of allenic alcohols has been applied to the synthesis of various natural products and analogs. Verrucosidin, citreoviridin, and their metabolite citreal have been prepared via an Ag-promoted stereoselective cyclization of a dihydroxyallene (Scheme 52).[91]

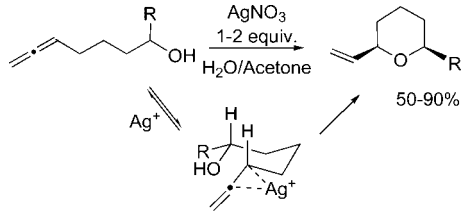
Prepared in two steps from Garner's aldehyde, a chiral protected 2-aminohepta-4,5-dien-1,3-diol was converted into the corresponding disubstituted *trans*-2,5-dihydrofuran upon treatment with stoichiometric amounts of silver nitrate in a mixture of acetone and water at room temperature. Chirality of the allene and the alcohol was preserved in the cyclization, as shown earlier by Marshall (see Scheme 46). Deprotection and oxidation of the alcohol led to (+)-furanomycin (Scheme 53).[98]

Similarly, the tetrahydrofuran motif of the cytotoxic amphidinolide X has been obtained by a Claesson's cyclization of 6-methylnona-4,5-dien-1,3-diol, derived from a chiral epoxyalcohol produced by the Sharpless asymmetric epoxidation (Scheme 54).[99]

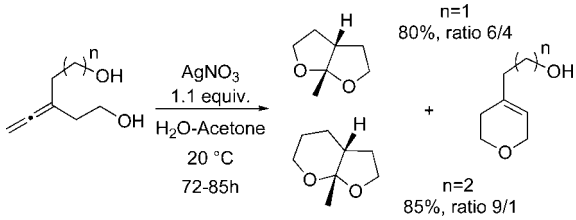
Scheme 48



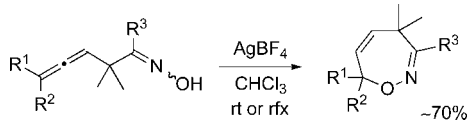
Scheme 49



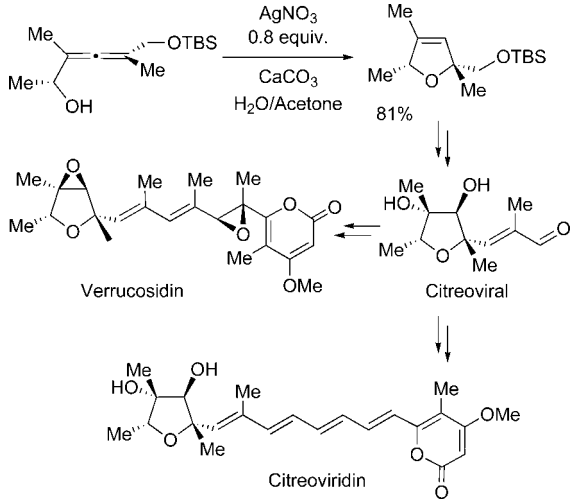
Scheme 50



Scheme 51

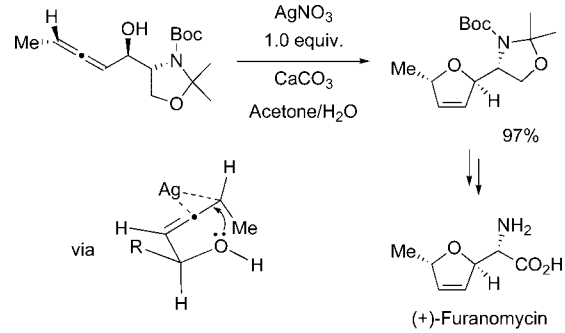


Scheme 52

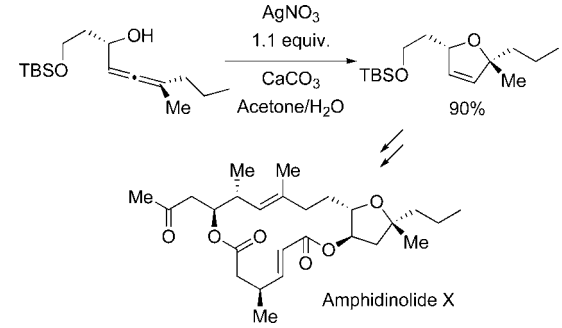


As a first approach toward the cembranoid eunicin, a silver mediated cyclization of a suitably functionalized allene was used with the goal of controlling the stereochemistry in the construction of the tetrahydropyran ring (Scheme 55). The *trans* bicyclic dihydro-2*H*-pyran within the tricyclic framework of eunicins was thus obtained starting from a 3-ethynylglucose derivative after diastereoselective formation of an allene through addition of pentenylmagnesium bromide, and silver nitrate promoted cyclization.[100]

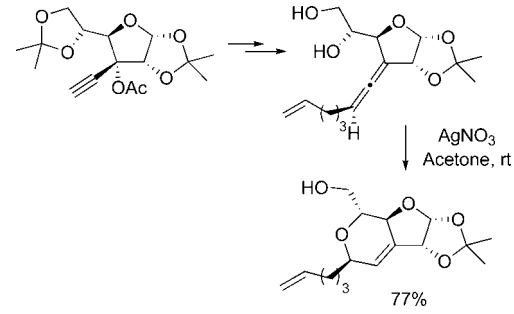
Scheme 53



Scheme 54



Scheme 55

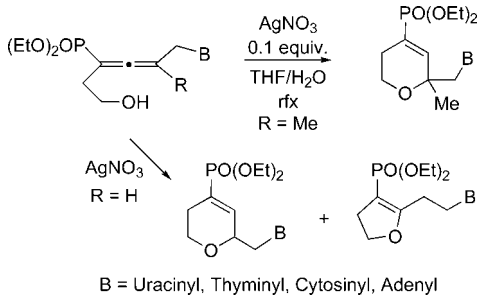


Unsaturated analogues of nucleosides have recently been obtained through the Ag-catalyzed cyclization of phosphonato β-allenic alcohols (Scheme 56).[101] Depending on the substitution of the allenic moiety, either dihydropyrans or a mixture of dihydropyrans and furans were produced.

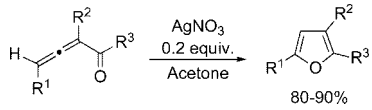
3.2.1.2. Cyclization of Allenones. In most Ag-promoted cyclizations, the oxygen atom which attacks as a nucleophile to the intermediate allenic π-complex belongs to an alcohol function. However, in some examples, the oxygen atom of ketone could also be engaged as a nucleophile as well as the oxygen atom of the carboxylic group.

Allenones have successfully been submitted to Ag-catalyzed cyclizations. Originally described with $AgNO_3$ or

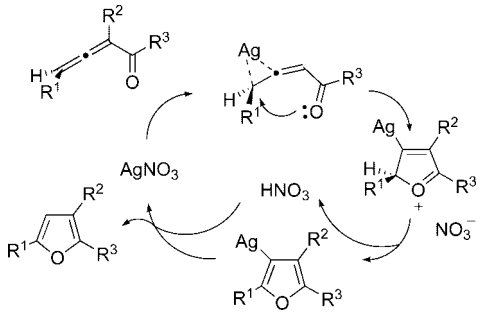
Scheme 56



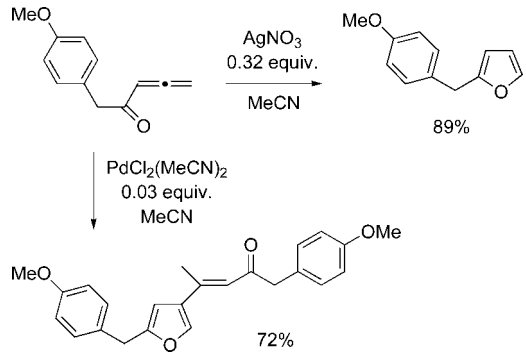
Scheme 57



Scheme 58



Scheme 59



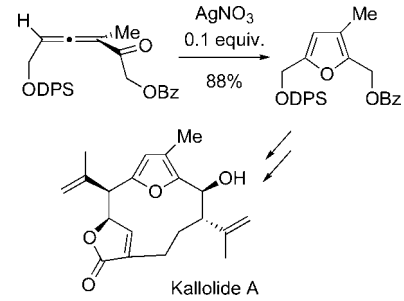
$AgBF_4$ in acetonitrile at 100 °C,[102] the cyclization of α-allenones to furans could be achieved in less drastic conditions by using a mixture of $AgNO_3$ and $CaCO_3$ as a catalyst in acetone/water at room temperature.[103,104] Later, Marshall et al. showed that $AgNO_3$ alone in acetone was able to rapidly yield furans (Scheme 57).[105]

The catalysis could be explained by a cascade of events including 5-*endo*-trig cyclization, aromatization, and acidolysis, the latter regenerating the catalyst (Scheme 58).

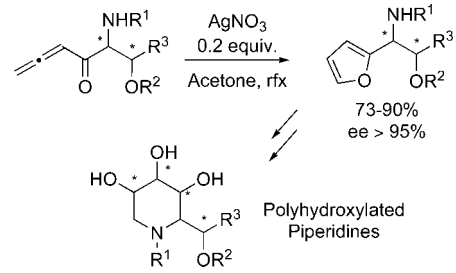
Interestingly, Hashmi et al. compared Ag- and Pd-catalyzed cyclizations of α-allenones. Although both reactions probably have the same π-complex intermediate, silver nitrate gave exclusively furans in good yields, whereas Pd^{II} mainly afforded a dimeric product resulting from cyclization and addition/carbometalation (Scheme 59).[106]

The cyclization of α-allenones was also successfully applied to total synthesis of natural products. The furanocembranes, kallolide A and B, were obtained through two Ag-catalyzed cyclizations as key steps.[107,108] In the synthesis of kallolide A, the first one was an allenone cyclization using

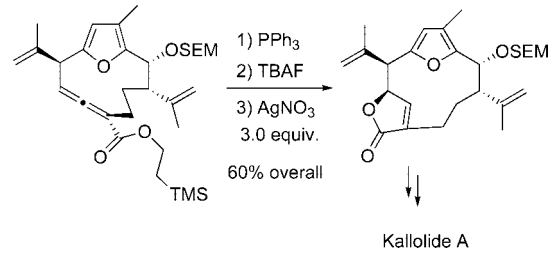
Scheme 60



Scheme 61



Scheme 62



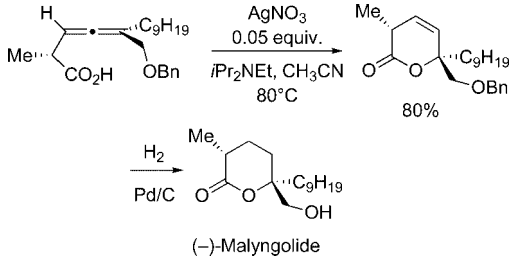
a catalytic amount of $AgNO_3$ in acetone, which led to a key furan building block in very good yields (Scheme 60). The second also used $AgNO_3$ for building the butenolide part of kallolide A, but this aspect will be discussed later.

Optically active furylaminoalcohols have been obtained from α-allenones derived from L-serine via a $AgNO_3$-catalyzed cyclization, and used as key precursors of biologically active polyhydroxylated piperidines (Scheme 61).[109]

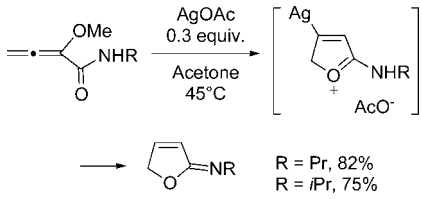
3.2.1.3. Cyclization of Allenoic Acids and Related Compounds. α-Allenoic acids proved to be also reactive with $AgNO_3$ in acetone at room temperature.[110] Interestingly, such cyclizations give butenolides, which are well-distributed motif in natural products. Kallolide A exhibits such a motif and its synthesis was based on the cyclization of an α-allenic acid in the presence of catalytic $AgNO_3$.[107] An isomerization of the intermediate allenic ester with triphenylphosphine was required to get the right geometry of the allenic moiety, before deprotection of the acid and cyclization to the corresponding butenolide (Scheme 62). The latter step nevertheless required an excess of silver reagent.

β-Allenic acids could also be cyclized in the presence of Ag salts as demonstrated in a short asymmetric total synthesis of (−)-malyngolide.[111] The δ-lactone motif of this natural product was obtained by submitting an optically active susbtituted β-allenic acid to catalytic $AgNO_3$ and substoichiometric quantity of soluble amine (Scheme 63). Interestingly, the chirality of the allenic moiety was preserved in this reaction. The 6-endotrig process was surprisingly preferred to the 5-*exo*-trig cyclization; the authors evoked a probably more stable transition state leading to the δ-lactone

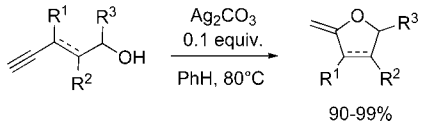
Scheme 63



Scheme 64



Scheme 65



compared to its homologue leading to furanone, the developing positive charge at the disubstituted allene terminus enhancing stabilization.

Interestingly, allenamides could also react in the presence of silver salt, but their behavior seems to be highly dependent upon the silver counterion as well as the substituents. With silver acetate in acetone, allenamides gave *O*-cyclization products (Scheme 64), while silver nitrate led to a mixture of *O*- and *N*-cyclization products (see section 3.3.1.3).[112]

3.2.2. With Alkynes

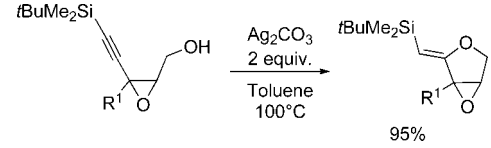
The Ag-catalyzed cyclization of acetylenic alcohols was also reported, but surprisingly, only a few examples are known. In contrast, the corresponding cyclization involving acetylenic acids is further described.

3.2.2.1. Cyclization of Alkynols. One of the pioneering examples of cyclization of alkynols is the silver-catalyzed synthesis of functionalized 2-methylene oxolanes from γ-acetylenic alcohols (Scheme 65).[113,114]

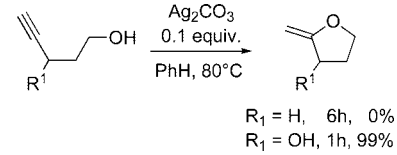
In sharp contrast with their behavior with the corresponding allenic alcohols, silver nitrate proved to be ineffective in this cyclization, while silver tetrafluoroborate only led to decomposition. However, silver salts having a basic counterion (silver acetate, oxide, and carbonate) gave the cyclization product in good to excellent yields. Silver carbonate proved to be the best catalyst, usually leading to quantitative yields without any decomposition. In these conditions, only the 5-*exo*-dig product was observed and only terminal alkynes could be efficiently cyclized. However, in the presence of twice the amount of silver carbonate and at a higher temperature, silylated alkynes could be exclusively converted to the corresponding *Z*-silyl enol ether (Scheme 66).

Interestingly enough, an activating effect of some substituents, especially oxygenated ones, at the propargylic position (R^1 in Scheme 65) was observed in this cyclization. Such propargylic substituents, probably altering the adjacent

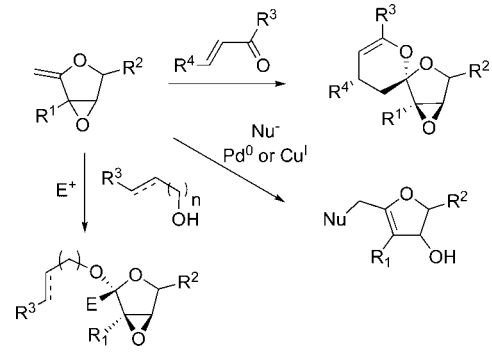
Scheme 66



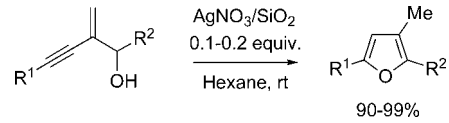
Scheme 67



Scheme 68



Scheme 69



π-system through hyperconjugation, led to a dramatic acceleration of the cyclization rate (Scheme 67).[115]

2-Methylene-3,4-epoxyoxolanes proved to be very interesting synthons, behaving either as enol ether or as vinylepoxide (Scheme 68). They can thus lead to stereodefined spiroketals, either through hetero-Diels−Alder reactions[116,117] or diastereoselective electrophilic additions[118] and radical cyclization.[119] They were also easily converted to furanes and dihydrofuranes by nucleophilic additions of cuprates or by Pd-catalyzed allylic substitutions.[120]

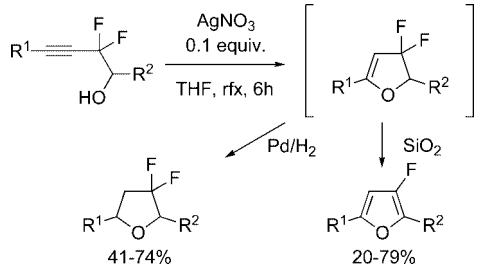
Related β-methylene alkynols could be cyclized to furans in the presence of silver nitrate, adsorbed on silica (Scheme 69).[121]

More recently, the strongly accelerating effect of propargylic substituent on the ring closure was applied to the synthesis of fluorofuran derivatives.[122] Fluoride substitution at the propargylic position of β-acetylenic alcohols allowed the formation of fluorohydrofurans by silver nitrate treatment (Scheme 70).

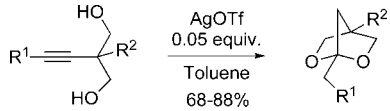
Working on ketal formations, Oh et al. very recently reported a convenient access to bridged bicyclic ketals, based on silver-catalyzed intramolecular oxycyclization of alkynes (Scheme 71). Silver triflate in toluene or dioxolane at room temperature proved to be the best catalyst for these double cyclizations.[123]

3.2.2.2. Cyclization of Alkynoic Acids. The silver-catalyzed cyclization of acetylenic acids was originally described as early as 1958 by Pascual's group.[124,125] This reaction was later studied in more detail by Pale and Dalla,[126,127] who found that silver carbonate in refluxing

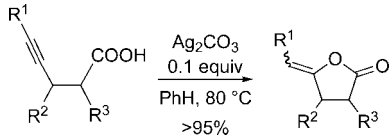
Scheme 70



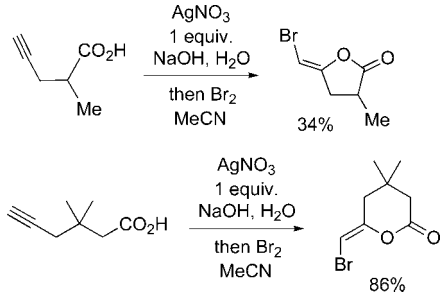
Scheme 71



Scheme 72



Scheme 73



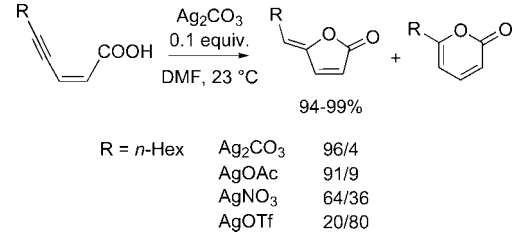
benzene was the best catalyst giving quantitative yields in most cases.[113] However, alkyl substituted alkynes led to a 1 to 1 mixture of *Z*/*E* isomers. As for acetylenic alcohols, the same accelerating effect of some propargylic substituents was observed in the cyclization of acetylenic acids (Scheme 72).[115]

Interestingly, Katzenellenbogen et al. were able to trap with bromine the intermediate organosilver formed upon cyclization. This led to a stereoselective access to *Z*-bromoenol lactones, but the yields remained modest, except when the Thorpe-Ingold effect favored cyclization (Scheme 73).[115]

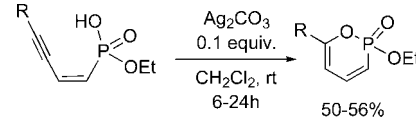
Conjugated enynoic acids readily react with silver salts, yielding furanones and/or pyranones depending on the salt and the susbtitutents.[125,128,129] Silver carbonate was again the best catalyst in this case, stereoselectively leading to *Z*-5-alkylidenefuran-2(^{5}H)-ones in excellent yields. A small fraction of the corresponding *2H*-pyran-2-ones were nevertheless produced, and as already reported,[113,114,127] the role of silver counterion proved to be critical for privileging the 5-exodig over the 6-endodig cyclization (Scheme 74). It is worth noting that zinc dibromide promoted the opposite situation, the *2H*-pyran-2-ones being the major product with this catalyst.[130]

More recently, it has been demonstrated that acetylenic phosphonic acids behave as their carboxylic anologues, leading to phospha analogues of 2-pyrones in the presence of silver carbonate (Scheme 75).[131]

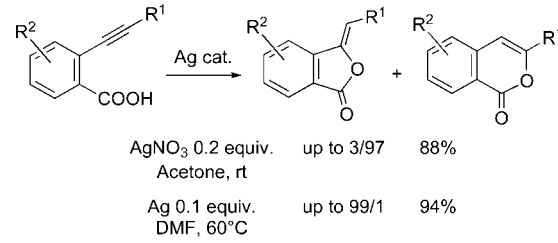
Scheme 74



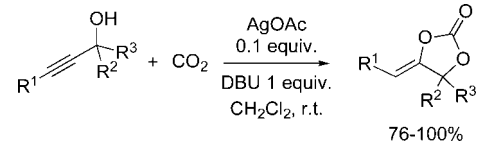
Scheme 75



Scheme 76



Scheme 77



Similarly, the benzo analogues, *o*-alkynylbenzoic acids, have been converted to the corresponding alkylidenebenzofuranones and/or isocoumarins (Scheme 76), through silver catalysis. Surprisingly, Ag powder in warm DMF proved to be the most selective conditions favoring the 5-*exo*-dig cyclization.[132]

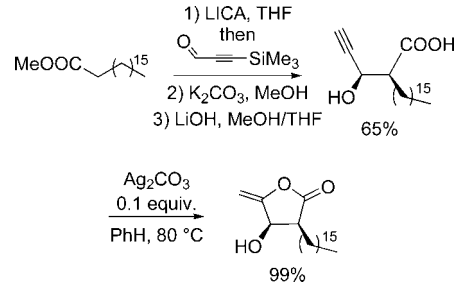
A very recent and interesting development of these cyclizations of acetylenic acids was the Ag-catalyzed reaction of acetylenic carbonates, in situ produced by carbonatation of propargyl alcohols (Scheme 77). In the presence of stoichiometric amount of DBU at room temperature in dichloromethane, most of the silver salts were efficient in promoting this reaction, leading to the exclusive formation of the alkylidene cyclic carbonates. However, only tertiary alcohols reacted, primary and secondary propargylic alcohols were not able to incorporate carbon dioxide.[133]

The silver-catalyzed cyclization of acetylenic acids offers a very efficient way to produce methylene or alkylidene lactones. Since such motifs are well distributed among natural and non-natural bioactive products, this reaction has been often applied to the total synthesis of such bioactive compounds.

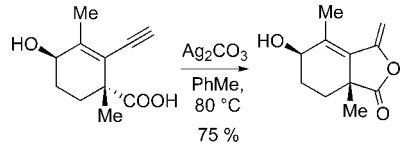
The first total synthesis of an antiappetent methylene lactone was achieved in only four steps with an overall yield of 64% with the silver-catalyzed cyclization of a substituted β-hydroxy-γ-acetylenic acid as the key step (Scheme 78). This synthesis allowed assigning the relative stereochemistry of the natural product.[134]

The Ag_2CO_3-catalyzed cyclization was also used in efficient syntheses of chiral dienes, key elements either for

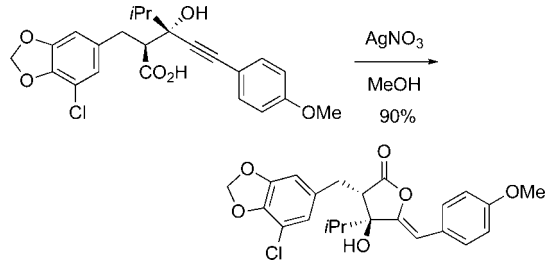
Scheme 78



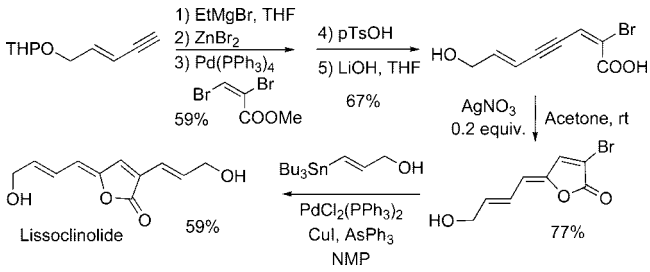
Scheme 79



Scheme 80



Scheme 81



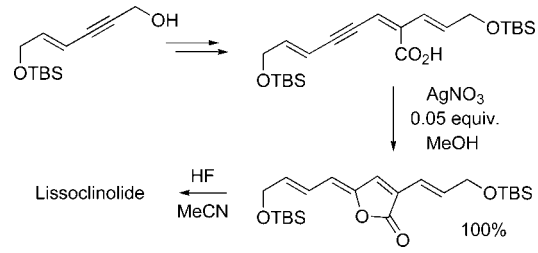
a Diels−Alder approach to kaura-9(11)-16-dien-19-oic acid (Scheme 79)[135] or for the synthesis of nagilactones.[136]

The antibiotic and algicidal cyanobacterin isolated from the freshwater cyanobacterium *Syctonema hofmanni* has been the subject of several total syntheses. Most of them relied on $AgNO_3$-catalyzed cyclization of an appropriate acetylenic acid, which allowed to efficiently and stereoselectively produce the benzylidene lactone structure of this antibiotic and of analogues (Scheme 80).[137,138]

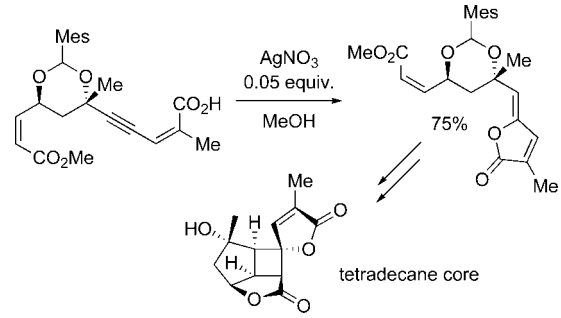
Among other γ-alkylidenebutenolides,[139] the highly conjugated lissoclinolide has been prepared through two routes, both elegantly relying on a combination of metal-catalyzed reactions including successive Pd-catalyzed coupling reactions and Ag-catalyzed cyclization. In one synthesis, protected (*E*)-pent-2-en-4-ynol was coupled with methyl 2,3-dibromoprop-2-enoate and the resulting bromodienyneester was converted into the corresponding acid and cyclized with silver nitrate in acetone. The alkylidene bromolactone so formed was then homologated by coupling again, yielding the natural product in only seven steps (Scheme 81).[140]

In the other synthesis, the monoprotected hex-2-en-4-yn-1,6-diol was homologated by Linstrumelle's coupling, then coupled with a vinylzirconocene, and homologated again to produce a trienyne acid. The latter was then quantitatively

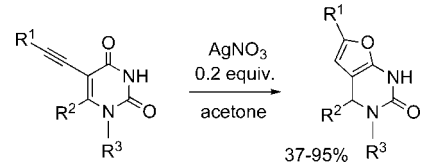
Scheme 82



Scheme 83



Scheme 84



cyclized upon treatment by methanolic silver nitrate (Scheme 82). Deprotection furnished the natural product in good overall yield (38% over seven steps).[141]

The novel [9.3.0.0^{2,10}] tetradecane ring system of the anticancer and antiparasitic bielschowskysin was ingeniously built up through a stereoselective [2 + 2] photocycloaddition of an alkenyl alkylidenebutenolide. The latter was obtained by a silver-catalyzed cyclization of the corresponding ynenoic acid (Scheme 83).[142]

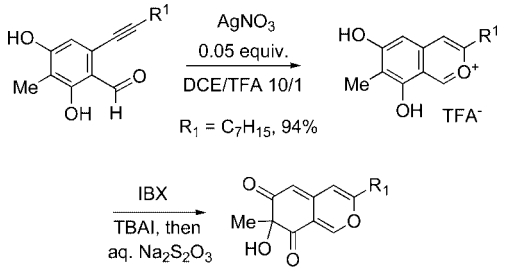
3.2.2.3. Cyclization of Alkynones and Related Compounds. Not only hydroxyl and acid groups, as described above, but also ketones can be involved in silver-catalyzed cyclization of acetylenic derivatives. A few examples revealed that, when placed at the right position, a keto group can act as nucleophile and add to the π-C−C bond activated by silver coordination.

This method offers an interesting and very efficient way to prepare modified nucleosides. Upon treatment with catalytic $AgNO_3$, 5-alkynyl uracil derivatives were almost quantitatively converted into their corresponding furanopyrimidine nucleoside analogues (Scheme 84).[143,144] Fluorescent uracil derivatives suitable for incorporation into the oligonucleotide mimic peptide nucleic acid (PNA) have been prepared through the same reaction.[145]

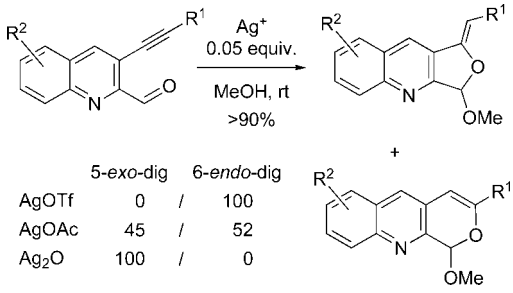
Together with gold triacetate, silver nitrate proved to be the best catalyst for the formation of benzopyrylium salts from *o*-alkynylbenzaldehydes (Scheme 85). After IBX oxidation, these salts gave azaphilones.[146]

Similarly, *ortho*-alkynyl formylquinolines have been cyclized by various silver salts. Surprisingly, either the 5-*exo*-dig product or the 6-endo product or both were produced depending on the silver counterion (Scheme 86).[147]

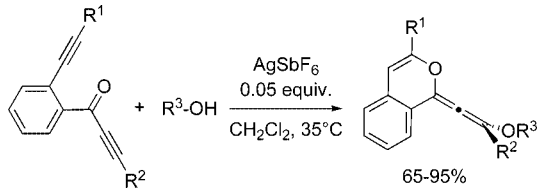
Scheme 85



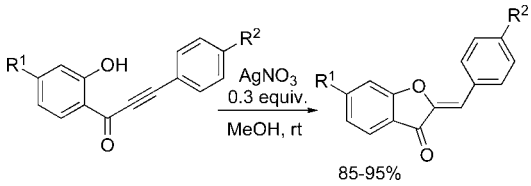
Scheme 86



Scheme 87



Scheme 88



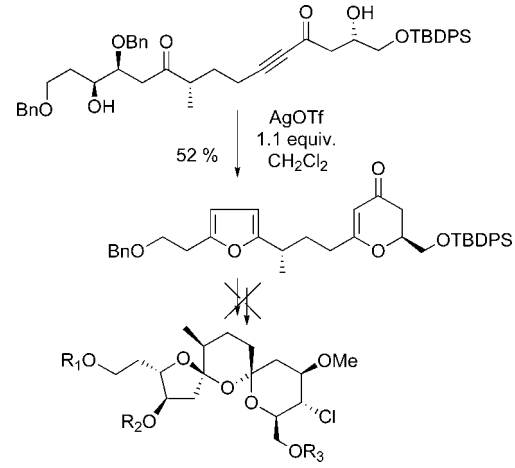
In a related process leading to the synthesis of 1-allenyl isochromenes, Yamamoto et al.[148] have elegantly combined a silver-catalyzed cyclization and the silver-catalyzed reaction of alkynones with alcohols (Scheme 87). The reaction most probably proceeds via the formation of benzopyrylium cation, which subsequently undergoes nucleophilic attack of an alcohol to give the annulation products.

Only few examples of intramolecular addition−cyclization reactions on ynone catalyzed by silver salts were reported. The first one was applied to the synthesis of aurones, a subclass of flavonoids, contributing to the pigmentation of flowers and fruits and exhibiting a variety of biological activities.[149] A catalytic amount of silver nitrate salt led efficiently to the 5-*exo*-dig cyclization of 3-aryl-1-[2-hydroxyaryl]prop-2-yn-1-ones into *Z*-aurones (Scheme 88).

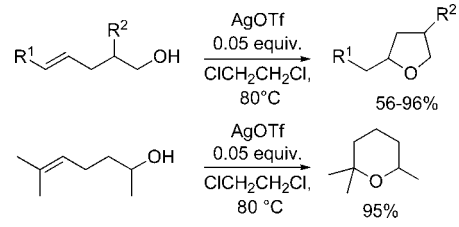
In the synthesis of the trioxadispiroketal unit of the phosphatase inhibitor spirastrellolide A, a hydroxylated ynone was cyclized in the presence of silver triflate (Scheme 89).[150] The yield was modest and a side reaction occurred on another part of the molecule, leading to a furan side chain.

Nevertheless, these results demonstrated that ynones represent another way of activating alkynes toward Ag-catalyzed cyclization.

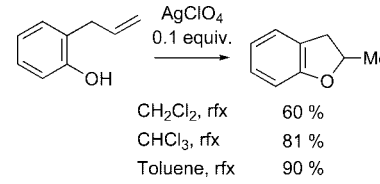
Scheme 89



Scheme 90



Scheme 91



3.2.3. With Alkenes

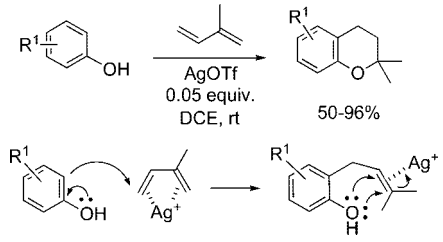
Only a handful of examples of Ag-catalyzed cyclizations implying hydroxyalkenes are known and all of them are recent, probably reflecting the popularization of silver salts as catalysts.

Intramolecular additions of alcohols and carboxylic acids to inert olefins have been achieved by treatment with silver triflate. δ-Alkenyl alcohols gave the 5-*exo*-trig product as the major or the only product, except with trisubstituted alkenes and terminal phenylalkenes, the reaction following a 6-*endo*-trig process (Scheme 90). For alkenyl acids, the cyclization mode seemed to depend on the chain length and the substitution. This reaction offered one of the simplest methods to construct cyclic ethers or lactones in good yields.[151]

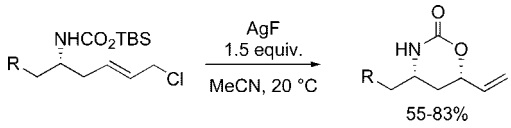
The same reaction was also applied to *o*-allylphenols with success. In this case, silver perchlorate in toluene proved to be a better catalyst than silver triflate.[152]

In an interesting extension, Eom et al. demonstrated that 1,3-dienes reacted with phenols in the presence of catalytic silver triflate, affording in good yields a variety of dihydrobenzopyran and dihydrobenzofuran systems (Scheme 92). From the product distribution, it looks like the sequential C−C and C−O bond formations occurring in this reaction started with the C-alkylation of the phenol by the Ag-activated diene. The resulting *o*-allylphenol could then cyclize following either 5-*exo*-trig mode or 6-*endo*-trig mode depending on the diene used.[153]

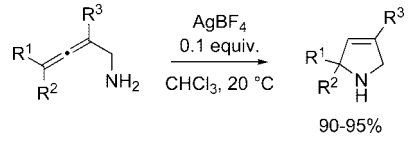
Scheme 92



Scheme 93



Scheme 94



Cyclic carbamates can be obtained from *tert*-butyldimethylsilyl carbamates bearing (*E*)-allyl chloride upon treatment by silver fluoride. In this method, the dual role of silver fluoride is clearly evidenced (Scheme 93). The fluoride ion unmasked the reactive carboxylate intermediate by desilylation, while silver ion activated the allyl chloride unit.[154]

3.3. Heterocyclization through C−N Bond Formation

Claesson and co-workers when attempting to purify allenic amines by GLC at 210 °C observed the complete conversion of *N*-benzyl 2,3-butadienamine into two new compounds, *N*-benzyl pyrrole and the corresponding 2,5-dihydropyrrole. Suspecting a metal-catalyzed process, they looked for the metal or its salt, which was responsible for this cyclization, and they ended up with silver salts.[84]

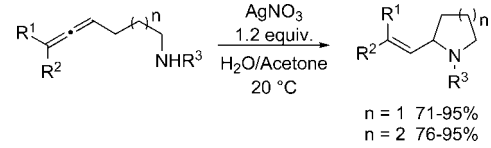
These results started an impressive series of works, addressing the scope of this allenic amine cyclization, investigating the mechanism and the stereochemical aspects of the cyclization as well as developing numerous applications to the total synthesis of natural products or related bioactive compounds. Pyrrole, pyridine, and their hydrogenated analogues are indeed largely represented among natural products, that is, alkaloids.

3.3.1. With Allenes

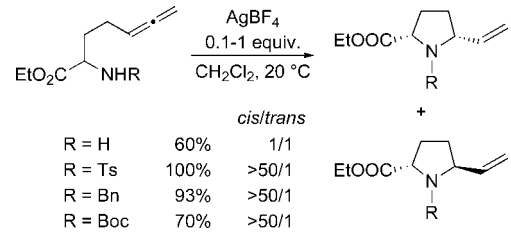
3.3.1.1. Cyclization of Allenamines. In their pioneering study, Claesson et al. showed that α-allenic amines could be very efficiently converted into 3-pyrrolines in the presence of catalytic silver tetrafluoroborate at room temperature (Scheme 94). The corresponding pyrroles were hardly detected (<3%).[84]

This original contribution was rapidly followed by several extensions by other groups, showing that the reaction was not limited to the formation of five-membered cycles. Among them, Arseniyadis and Goré interestingly compared the role of mercuric and silver salts on the cyclization of γ- and δ-allenic amines. This contest was largely in favor of the silver salts. The $AgNO_3$-catalyzed cyclization required only 5 h at room temperature in a single and simple step, while

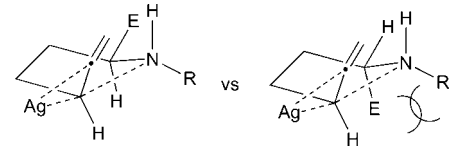
Scheme 95



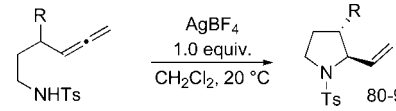
Scheme 96



Scheme 97



Scheme 98



the $HgCl_2$-catalyzed version required 12 h at 60 °C and a reductive workup to cleave the Hg−C bond of the organomercuric compounds produced. The yields were always better with $AgNO_3$ than with $HgCl_2$ (71−95 and 35−70%, respectively). As for the alcohol version (see section 3.2.1.1), this cyclization was regioselective, always providing the 5- or 6-*exo*-trig products, but also stereoselective, giving the *E*-isomer when the starting allene was 1,3-disubtituted (Scheme 95).[155,156]

The stereochemical aspects of the cyclization of allenic amines have been studied by Gallagher et al. They demonstrated at γ-allenic α-aminoesters readily cyclized in the presence of silver tetrafluoroborate, giving *cis*-2,5-disubstituted pyrrolidines with high selectivity. The presence of a bulky group on the nitrogen atom proved to be essential for this selectivity, since without it, there is no selectivity at all (Scheme 96).[157,158]

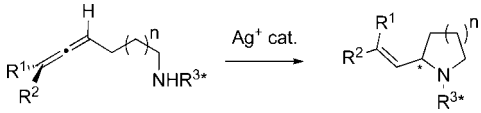
The fact that the size of the *N*-susbtituent rather than its electronic effect plays a key role suggests a envelope-like transition state, where the ester group would be better placed in an equatorial position and *anti* to the *N*-substituent (Scheme 97).

When the susbtituent was adjacent to the allene moiety, *trans*-2,3-pyrrolidines were obtained in excellent yield and diastereoselectivity.[159] However, the reaction now required 1 equiv of silver salt (Scheme 98). The stereochemistry can be rationalized with the same model as Scheme 97.

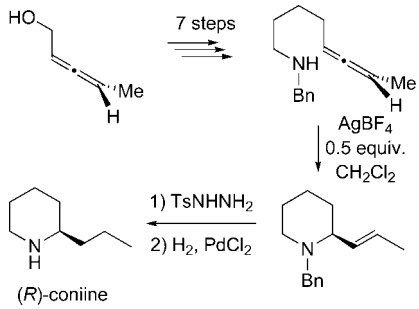
These stereochemical studies culminated with chiral versions. With allenic amines as substrates, it was clearly tempting to either use the intrinsic chirality of the allenic moiety or to place a chiral auxiliary on the reacting amino group to produce chiral *N*-heterocycles (Scheme 99). The key questions were thus the following:

(i) Will the allene chirality be transferred to the newly created substituted C−N bond?

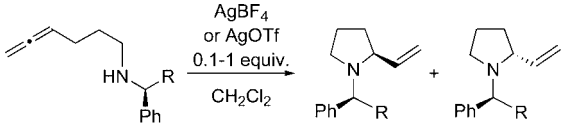
Scheme 99



Scheme 100



Scheme 101



R = Me	87%	2/1
R = CO_2Me	71%	4/1
R = CH_2OH	90%	4/1
R = CH_2NHMe	70%	8/1
R = CONHMe	90%	9/1
R = CH_2SPh	90%	13/1
R = $CH_2S(O)Ph$	90%	99/1

(ii) Would a chiral auxiliary on the reacting amino group induce chirality during the formation of the C−N bond ?

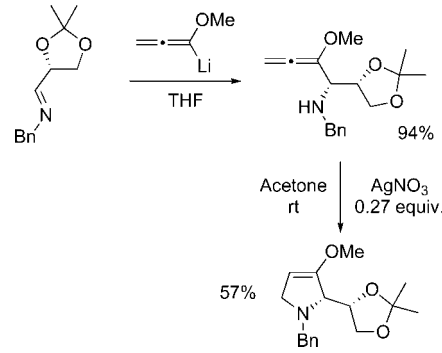
Both have been addressed, mainly by Gallagher's group again. The first question was answered through a rapid and efficient synthesis of (*R*)-(−)-coniine. The (*R*)-(−)-*N*-benzylocta-5,6-dienylamine (80% ee) was cyclized by treatment with $AgBF_4$ and the *N*-benzyl-2-propylydenepiperidine so obtained was reduced. The resulting coniine exhibited an ee of 78%, indicating an excellent transfer of chirality, with nevertheless a small racemization during this process.[160]

The second question was addressed in varying the nature of the substituent in the phenethyl type auxiliary used (Scheme 101). The results showed that a good diastereoselectivity (up to 80% de) could be achieved with coordinating substituents, especially with amide and thio groups, in a noncoordinating solvent. Surprisingly, the diastereoselectivity proved to be also dependent on the Ag catalyst concentration, suggesting a more complex mechanism involving several molecules of allenic amines.[161,162] Playing with these factors, an almost complete induction was obtained with a phenethyl auxiliary carrying a sulfoxide group.[163]

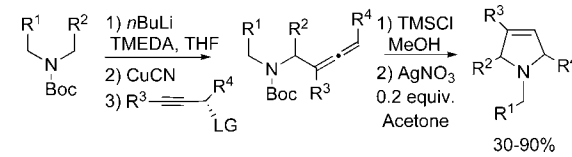
More recently, the Claesson-Goré's cyclization was applied to various optically pure aminoallenes leading to substituted Δ^3-pyrrolines. Aminoallenediols, obtained by addition of lithiated methoxyallene to imines derived from (*R*)-glyceraldehyde or malic acid, afforded the corresponding pyrrolines upon treatment with silver nitrate (Scheme 102).[164]

α-(*N*-Carbamoyl) allenes obtained in two steps by *ortho*-lithiation of amine and alkylation with propargyl derivatives rapidly led to Δ^3-pyrrolines upon treatment with $AgNO_3$ in acetone (Scheme 103).[165–167] In a closely related work, allenic aminoacids were cyclized in the same conditions.[158]

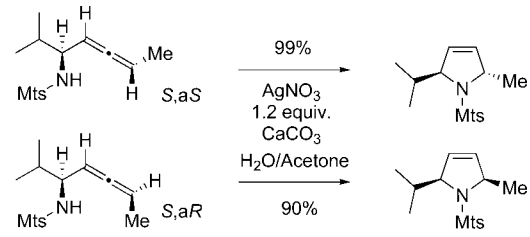
Scheme 102



Scheme 103

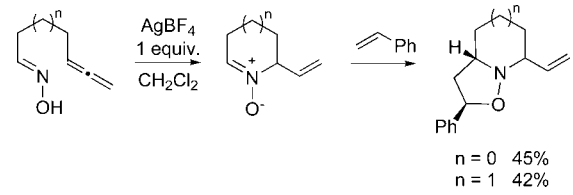


Scheme 104



Mts = 2,4,6-trimethylbenzenesulfonyl

Scheme 105



Similarly, enantiopure *N*-sulfonylated amino allenes prepared from natural α-aminoacids stereospecifically yielded the pyrroline derivatives upon treatment with silver salts such as $AgBF_4$ and $AgNO_3-CaCO_3$ (Scheme 104).[168]

3.3.1.2. Cyclization of Allenimines and Oximes. Nitrogen nucleophiles other than amines could be involved in Ag-mediated cyclizations.

In a logical extension, Gallagher et al. studied the cyclization of allenic oximes and found that silver tetrafluoroborate usually promoted the *N*-cyclization, which gave cyclic vinyl nitrones. Unstable, the latter could be trapped by various alkenes, leading to complex bicyclic frameworks with high stereoselectivity (Scheme 105).[169,170]

Even hexahydroazepine ring system could be produced in good yields providing that maleimide was used as trapping alkene (Scheme 106).[171]

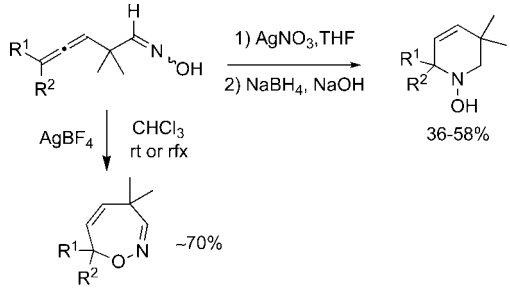
Interestingly enough, the cyclization mode proved to be highly dependent on the oxime stereochemistry, the *E* giving the cyclic vinyl nitrone, while the *Z* led to *O*-cyclization and gave vinyl oxazines (Scheme 107).[170,172]

It may not be that simple since Grimaldi et al. found in parallel that using $AgNO_3$ in aqueous THF instead of $AgBF_4$ in chloroform[97] led exclusively to the six-membered rings

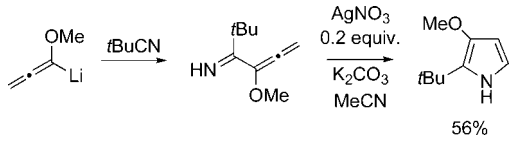
Scheme 106

Scheme 107

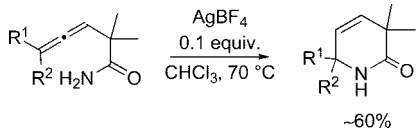
Scheme 108



Scheme 109



Scheme 110



which are subsequently in situ reduced with sodium borohydride giving 1-hydroxy-1,2,3,6-tetrahydropyridines (Scheme 108).[173]

More simple imines could also be involved as nucleophile in Ag-catalyzed cyclization. Indeed, addition of lithiated methoxyallene to pivalonitrile afforded iminoallene, which was cyclized upon treatment with silver nitrate to the corresponding pyrrole derivative.

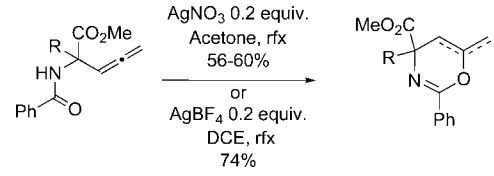
3.3.1.3. Cyclization of Allenamides and Related Compounds. Amides could also be engaged in Ag-catalyzed cyclizations. With the same catalyst as Claesson et al. but at reflux, β-allenic amides surprisingly gave 3,6-dihydro-2-pyridones (Scheme 110).[175] These compounds resulted from 6-*endo*-trig cyclization where the nitrogen of the amide acted as nucleophile.

It is worth noting that *N*-benzoyl allenic aminoacids led to *O*-cyclization instead of the expected *N*-cyclization upon treatment with $AgNO_3$ or $AgBF_4$ (Scheme 111).[158]

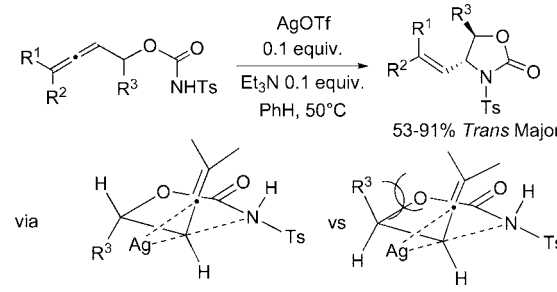
With a shorter chain, a mixture of *O*- and *N*-cyclization products were formed when allenamide was submitted to silver acetate or nitrate in acetone (see section 3.2.1.3).[112]

Carbamates have also been implied in Ag-catalyzed cyclizations. In the presence of silver isocyanate or triflate and of base, *O*-2,3-butadienylcarbamates cyclized to the corresponding vinyloxazolidinones. The nature of the group carried by the nitrogen atom as well as the nature of the

Scheme 111



Scheme 112



base played critical roles in this cyclization (Scheme 112). A modest to high stereocontrol (20 to 99% de) in favor of the *trans* isomer was observed, the larger the susbtituent R_3, the higher the selectivity. 3,4-Pentadienyl tosylcarbamates similarly gave 4-vinyltetrahydro-2*H*-1,3-oxazin-2-ones with higher *trans* selectivities.[176,177] These results suggested a transition state, very similar to those already proposed for the formation of *cis*-2,5-disubstituted pyrrolidines and *trans*-2,3-pyrrolidines (See Scheme 97).

With its convergence, its stereochemical properties and its power, it is not a surprise to have Ag-promoted *N*-heterocyclization, applied in total synthesis. Various examples, from simple alkaloids to more complex compounds, have been reported.

The simplest structure obtained was probably the coniine, an alkaloid found in hemlock poison and yellow pitcher plants. However, this was one of the first chiral synthesis in this area, and the (*R*)-(−)-coniine was produced (see section 3.3.1.1, Scheme 100).[160]

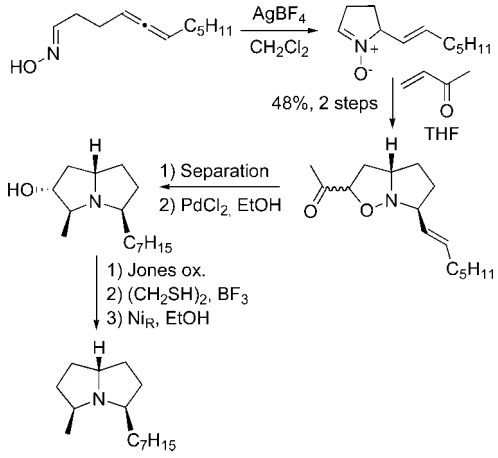
The nitrone synthesis and its in situ trapping developed by Gallagher et al. have been applied to the synthesis of pyrrolizidine alkaloids. For example, a component of the venom of the ant *Solenopsis xeroveneum*, 3α,5α,7αβ-hexahydro-3-heptyl-5-methyl-*1H*-pyrrolizidine, has been prepared starting with the Ag-catalyzed cyclization of (*E*)-undeca-4,5-dieneoxime. The resulting nitrone was trapped by methyl vinyl ketone furnishing a 1:1 mixture of diastereoisomers, which were separated, reduced, and deoxygenated (Scheme 113).[172]

The antibiotic anisomycin has been obtained through a sequence, in which the Ag-catalyzed cyclization of an alkoxyaminoallene was the key step (Scheme 114).[178]

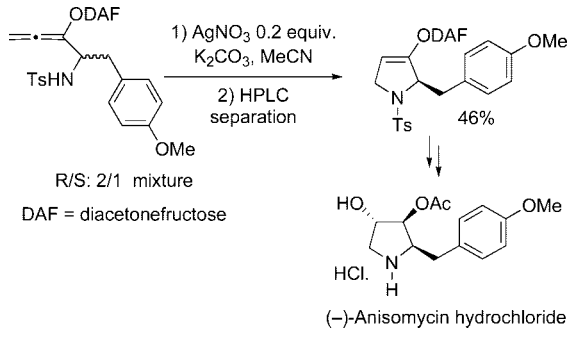
The total synthesis of clavepictines, antibiotic and antitumor quinolizidine alkaloids isolated from a tunicate, was cleverly designed and realized with Ag-catalyzed cyclization of a piperidinoallene as the key step (Scheme 115). Control of the configuration of allenes imposed a favored transition state, which afforded the desired *cis*-quinolizidine derivative in 48% yield. Only 7% of vinyl isomer was formed though loss of chirality transfer.[179]

Modifying the substrate significantly improved the cyclization yield as well as the diastereoselectivity, and no other isomer was detected (Scheme 116).[179]

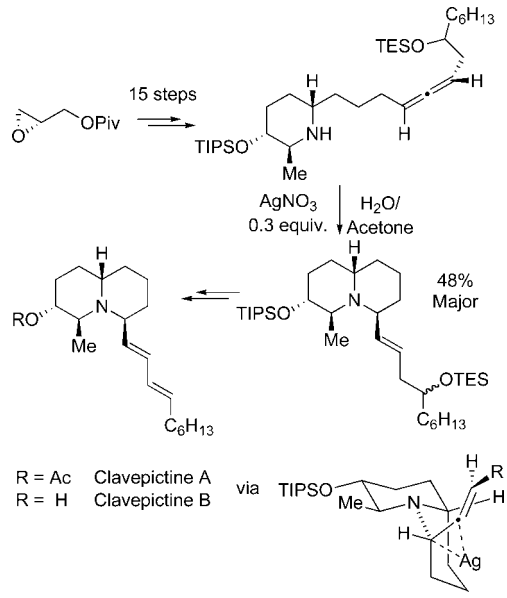
Scheme 113



Scheme 114



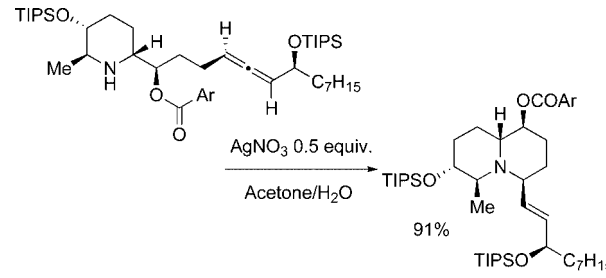
Scheme 115



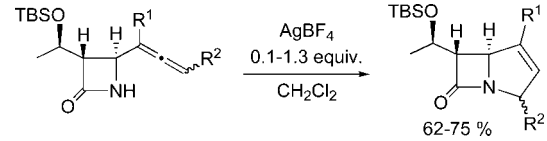
An interesting and stereoselective synthesis of 3-substituted carbapenems was based on an Ag-mediated cyclization of allenic azetidinones (Scheme 117).[180]

Surprisingly, when a stereodefined allene was used, the stereoselectiviy of the cyclization varied upon the silver amount present in the reaction and could even been reversed (Scheme 118). Such complex phenomena are reminiscent of those described by Gallagher et al. in their study of the Ag-catalyzed cyclization of allenic amines carrying a chiral auxiliary (see Scheme 101). Diastereoselectivity proved to be also dependent on the Ag catalyst concentration, and as

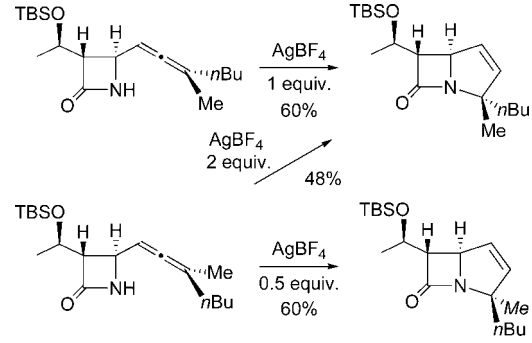
Scheme 116



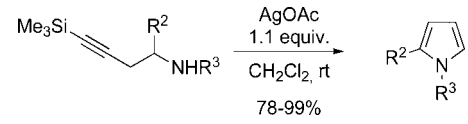
Scheme 117



Scheme 118



Scheme 119



mentioned there, this could be indicative of a more complex mechanism.

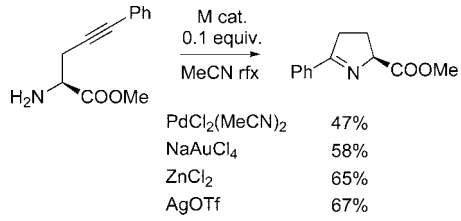
3.3.2. With Alkynes

Surprisingly, only a few examples of Ag-catalyzed cyclization of aminoacetylenic derivatives are known and most of them are recent.

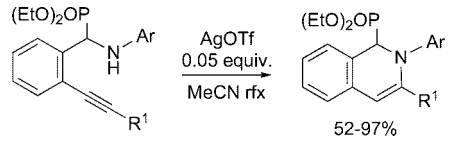
Pyrroles can conveniently be obtained from homopropargyl amines upon treatment by silver acetate (Scheme 119). This reaction probably occurs via an intramolecular addition of the amine to the acetylenic moiety through a 5-*endo*-dig cyclization. The resulting dihydropyrrole is probably oxidized either by air or due to the stoichiometry, by silver ion. Since the starting homopropargyl amines are readily available by addition of propargyl Grignard reagents to Schiff bases, this sequence offered a rapid access to pyrroles and can be applied to cyclic imines, such as 3,4-dihydro-β-carboline, leading after cyclization to complex alkaloids such as indolizinoindole alkaloids.[181]

Usually working on Pd-catalyzed formation of pyrrolidines from alkynyl amines, Rutjes et al. found that this reaction is better performed in the presence of silver triflate as catalyst (Scheme 120). They thus applied this cyclization to an interesting two-step synthesis of 5-arylated prolines, starting from propargyl glycines.[182]

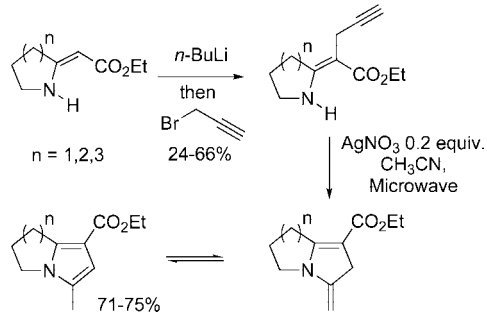
Scheme 120



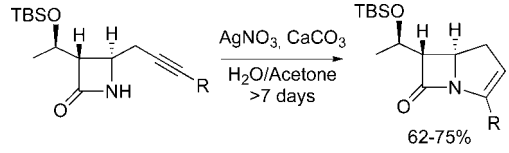
Scheme 121



Scheme 122



Scheme 123



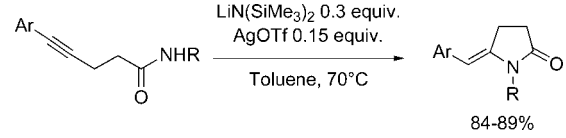
Interestingly, alkynylaminophosphonates analogue to α-aminoacids could also be cyclized in the presence of silver triflate. With a benzo group within their alkynyl chain, these compounds led to 1,2-dihydroisoquinolines in high yields, through a 6-*endo*-dig process. An extensive screening of catalysts revealed that $PdCl_2(PhCN)_2$ exclusively catalyzed the concurrent 5-*exo*-dig cyclization, leading to substituted isoindoles.[183]

In an interesting extension, Dovey et al. described the Ag-catalyzed cyclization of propargyl enaminoesters, obtained by *C*-propargylation of cyclic vinylogous carbamates using *n*-butyllithium (Scheme 122). In this reaction, the stereochemistry of the starting enaminoesters was obviously reversed, but this aspect was not addressed. This reaction has been applied to the synthesis of the pyrrole analogues of pyrrolizidines, indolizidines, and pyrroloazepines.[184,185]

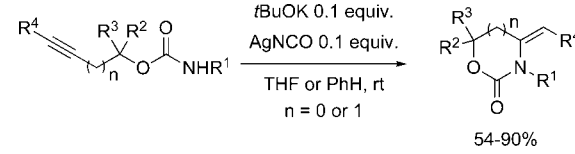
In their work on the synthesis of 3-substituted carbapenems, Liebeskind and Prasad showed that 4-propargyl azetidinones could be cyclized in the presence of silver salts. This reaction is similar to the one described with allenic azetidinones, but in this case silver nitrate, instead of silver tetrafluoroborate, gave better yield.[180]

This example also revealed that amides could also act as a nucleophile in Ag-catalyzed heterocyclization. In the other sole example, an alkynyl amide was cyclized in the presence of silver triflate with high selectivity in favor of the *E*-isomer, but the reaction required the deprotonation of the amide prior to cyclization, and quite harsh conditions were used (Scheme 124).[186,187]

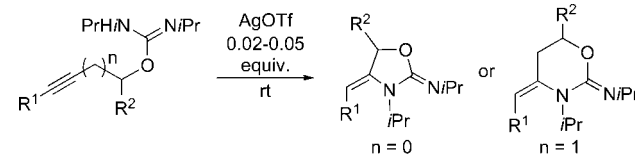
Scheme 124



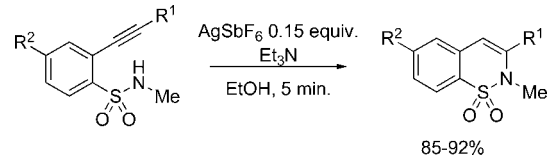
Scheme 125



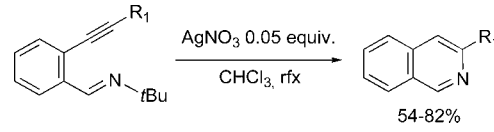
Scheme 126



Scheme 127



Scheme 128



As for allenes, carbamates could also be involved in the Ag-catalyzed heterocyclization of aminoalkyne derivatives. The NH-part of *O*-propargylcarbamates reacted with the acetylenic moiety after activation with silver isocyanate and a strong base (*t*BuOK), yielding methylene oxazolidinones (Scheme 125). It is worth noting that the same reaction could also be promoted by copper chloride. In this case, depending on the nature of the group carried by the nitrogen atom, a mild (NEt_3) or a strong base (*t*BuOK) was required.[188]

In a similar way, acetylenic isoureas gave oxazolidines or oxazines when treated with silver triflate (Scheme 126). No yield was reported in this publication.[189]

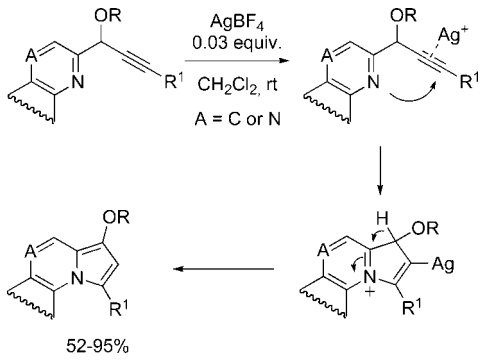
Very recently, benzenesulfonamides were also cyclized by silver salts, selectively giving 1,1-dioxo-2*H*-1,2-benzothiazines (Scheme 127). Yields were higher than 80% in DMF or ethanol and no *O*-cyclization was detected. Silver nitrate, fluoride, and hexafluoroantimonate proved to be better catalysts than copper(I) salts. $AgSbF_6$ associated to triethylamine remarkably reduced the reaction time without affecting the efficiency of the reaction.[190]

In reactions similar to those implying *ortho*-alkynyl benzaldehydes, imines derived from these substituted benzaldehydes could be cyclized in the presence of silver salts. Substituted isoquinolines have indeed be obtained from *ortho*-alkynyl benzaldimines under mild conditions (Scheme 128).[191]

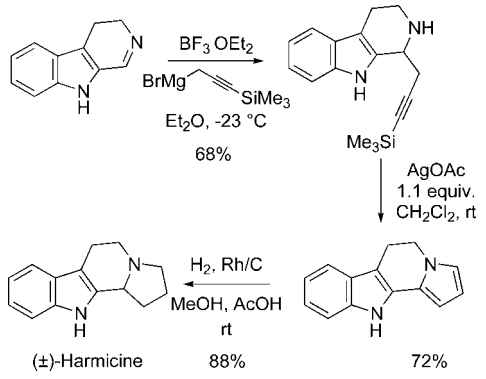
Cleverly, the iminium intermediate produced in such cyclizations has been trapped by various pro-nucleophiles, and even by silver acetylides, in situ produced from added terminal alkynes (Scheme 129).[192]

Scheme 129

Scheme 130



Scheme 131



In a similar way, sp^2 nitrogen atoms embedded in aromatic compounds also reacted with alkynes in order to give *N*-fused heteroaromatic compounds via an intramolecular cyclization catalyzed by $AgBF_4$ or $AgPF_6$ (Scheme 130). Other catalysts were also examined but silver salts were far more efficient than copper, gold, palladium, platinum and other salts. Deuterium-labeling experiments gave some hints on the mechanism of this reaction.[193]

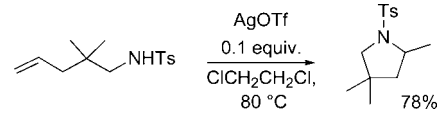
The indolizinoindole alkaloid harmicine, extracted from the leaves of a Malaysian plant and exhibiting strong antileishmania activity, has been obtained in only four steps from tryptamine via a silver mediated cyclization (Scheme 131).[194]

3.3.3. With Alkenes

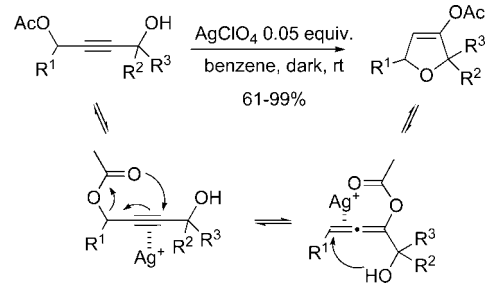
The number of Ag-catalyzed cyclization involving aminoalkenes is even more reduced than those with aminoalkynes.

An intramolecular hydroamination of unactivated olefins has been achieved by catalysis with silver triflate (Scheme 132). An extensive catalyst screening revealed that iron chloride was the most effective, quantitatively leading to 2,4,4-trimethyl-1-(toluenesulfonyl)pyrrolidine in only 2 h, while silver triflate required 16 h for 78% yield.[195]

Scheme 132



Scheme 133



3.4. Heterocyclization through Rearrangement Reactions

A few reaction cascades involving silver catalysts are known and they were collected in this section. All of them relied on in situ formation of acyloxyallenes (allenyl acetate) from α-acyloxyalkynes through [3,3]-sigmatropic rearrangement, known to be catalyzed by silver salts.[196]

Applied to monoacetyled butynediols, substituted 2,5-dihydropyrans were obtained by a cascade of reactions involving first the silver-catalyzed rearrangement and second a silver-catalyzed allenol cyclization.[197,198] Reactions were routinely run in the presence of 5% of silver perchlorate or silver tetrafluoroborate in refluxing benzene (Scheme 133).

Racemic natural products like bullatenone, geiparvarin,[198] and ascofuranone[199] were prepared by this strategy.

Quantitative chiral transfer was nevertheless achieved starting from an enantio-enriched propargyl ester. This version was applied to the synthesis of (−)-ascofuranone, and the chirality was introduced by the asymmetric reduction of an alkynone with (*S*)-alpine borane (Scheme 134).[200]

In a similar way, α-allenones have been very recently produced in situ as intermediate and cyclized to substituted furans (Scheme 135).[201,202] On the basis of the known Ag-catalyzed 3,3-sigmatropic rearrangement,[199,203] the authors obtained in situ α-allenones from α-alkynylketones bearing at the propargylic position either acyloxy, sulfonyloxy, or phosphate groups. The same catalyst, which promoted the 3,3-sigmatropic rearrangement, also catalyzed the cycloisomerization.

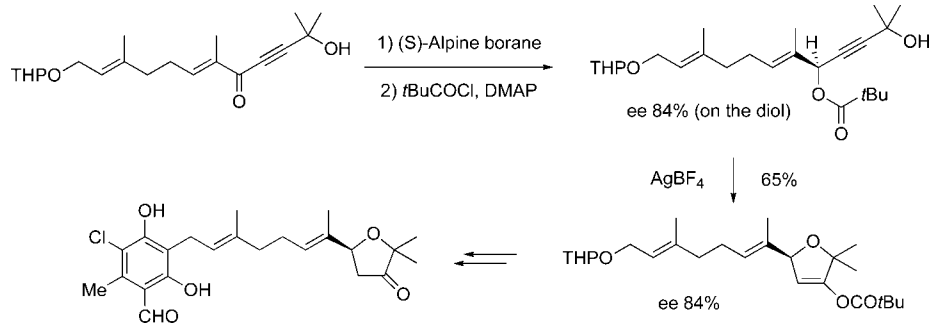
While working on an original strategy for the construction of spirocyclic 3(2H)-furanones, Kirsch et al. discovered that $AgSbF_6$ was able to catalyze the rearrangement of α-hydroxyalkynones (Scheme 136). This process is probably initiated by a Ag-catalyzed cyclization, and the so-formed cyclic oxonium ion rearranged in furanone via an alkyl 1,2-migration.[204]

4. Conclusion

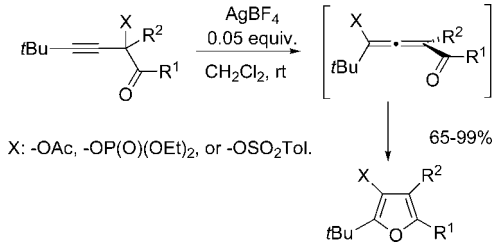
The results detailed in this review clearly showed that silver ions are very powerful and efficient catalysts for cross-coupling reactions, as well as for heterocyclization reactions.

In cross-coupling reactions, silver salts play a dual role. They can abstract halides from organometallic intermediates, rendering the metal more electropositive and opening a vacant site in the coordination sphere. In these cases, the

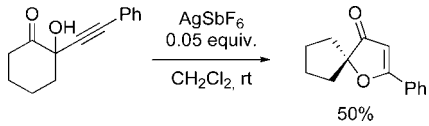
Scheme 134



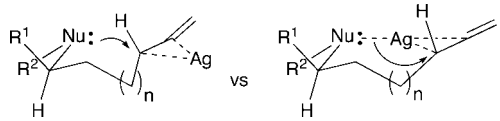
Scheme 135



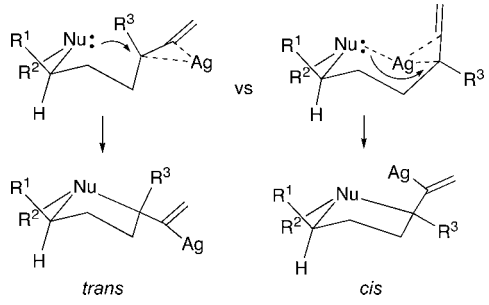
Scheme 136



Scheme 137



Scheme 138



main role is thus to form insoluble silver halides while activating the actual catalytic species. These phenomena have mainly been applied to Heck, Stille and Suzuki reactions. With some starting materials, especially alkynes, silver salts can produce organosilver species, which can either react as such or more often be transmetalated to various metals or organometallics, especially organopalladium intermediates.

Silver-catalyzed heterocyclizations provide a very efficient access to an impressive variety of substituted *O*- and *N*-heterocycles.

From a mechanistic point of view, heterocyclizations correspond to electrophilic additions, the silver ion being the electrophile. They thus usually follow Baldwin rules and produced the shortest heterocycle possible through *exo*-cyclization, except if steric or electronic effects shift the process toward *endo*-cyclization and thus toward larger rings.

More complex mechanism cannot be ruled out, especially when the nucleophile is a nitrogen atom. The well-known ability of amines and related nitrogen derivatives to coordinate Ag ion suggests the intermediate formation of complexes π-Ag−N, which could rearrange by reactions in the inner coordination sphere (Scheme 137).

Whatever the mechanism, the stereochemical outcome of heterocyclization clearly depends on substitution pattern and ring size. Envelope and chairlike transition states usually give reasonably correct predictions of the heterocycle stereochemistry (Scheme 138).

5. References

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