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Recent Advances on the Lewis Acid-Catalyzed Cascade Rearrangements of Propargylic Alcohols and Their Derivatives

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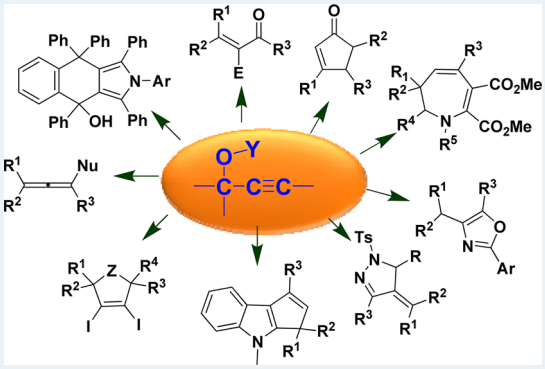
ABSTRACT: Propargylic alcohols and their derivatives are important classes of organic compounds that can be easily accessible from terminal alkynes and aldehydes or ketones. They are attractive and have been extensively applied as synthetic intermediates in modern organic synthesis. Recent investigations on the chemistry of propargylic alcohols and their derivatives disclosed a variety of highly efficient Lewis acid-catalyzed cascade reactions based on Meyer−Schuster rearrangement of propargylic alcohols and [3,3] rearrangement of propargylic esters and propargyl vinyl ethers. A tremendous number of structurally versatile enones, carbocycles, and heterocycles have been constructed through these methodologies. These advances, including our recent researches in this field, are summarized in this review.



KEYWORDS: *cascade reactions, Meyer-Schuster rearrangement, propargylic alcohols, allenic carbocations, [3,3] rearrangement*

1. INTRODUCTION

The classical Meyer−Schuster rearrangement of propargylic alcohols (**1**), furnishing the corresponding α,β-unsaturated aldehydes or ketones (**2**) via a 1,3-shift of the hydroxyl group from **A** to allenol **B** in the presence of Brønsted acid or Lewis acid (Scheme 1, eq 1), was first reported by K. H. Meyer and K. Schuster in 1922.[1] This reaction has been extensively applied in organic synthesis due to high atom economy and high efficiency for converting readily available materials into versatile enone products. A closely related acid-catalyzed rearrangement of propargylic alcohols afforded α,β-unsaturated ketones (**3**) via a formal 1,2-shift of the hydroxy group through enyne **C**, which was called the Rupe rearrangement (Scheme 1, eq 2). Swaminathan and Dudley have reviewed the Meyer−Schuster rearrangement and its synthetic applications in the synthesis of α,β-unsaturated carbonyl compounds.[2] Recently, the chemistry of propargylic alcohols and their derivatives has attracted much attention and has been extensively investigated. One sign of significant progress in this field is the development of approaches to versatile allene derivatives (**4**) through trapping the allenic carbocation intermediates (**F**) generated from propargylic alcohols with a variety of nucleophiles (Scheme 1, eq 3). In these cases, the 1,3-hydroxyl shift in the classic Meyer−Schuster rearrangement was effectively inhibited by using the stronger nucleophiles. More importantly, the *in situ*-generated allenes (**4**) could undergo various cascade processes to furnish structurally interesting carbocycles or heterocycles. A major shortcoming of the classic Meyer−Schuster rearrangement is the selectivity among many possible competing pathways (e.g., Rupe rearrangement). One way that this rearrangement can predominantly occur is through the activation of carbon−carbon triple bond (C≡C) with a late transition metal, which is called a "soft" Lewis acid (Scheme 1, eq 4). The transition-metal catalyst can coordinate the π-system of the alkyne to form the α-metal-α,β-unsaturated carbonyl intermediate (**H**), which can be converted into the enone products (**5**) in the presence of electrophile. Recent catalytic developments have enabled this process to be controlled in such a fashion that the enones can be formed in good yields and high stereoselectivities. Additionally, it was also demonstrated that propargylic esters and propargyl vinyl ethers could undergo the [3,3] rearrangement, followed by electronphilic substitution and subsequent hydrolysis to furnish enones **5** with high stereoselectivity (Scheme 1, eq 5). In this review paper, we would like to summarize the recent advances on these transformations.

2. CASCADE REACTIONS OF PROPARGYLIC ALCOHOLS VIA ALLENIC CARBOCATION MECHANISM

2.1. Trapping Allenic Carbocation with Electron-Rich Arene. It has been demonstrated that the electron-rich arenes could capture the allenic carbocation **F** (Scheme 1, eq 3) to form a Friedel−Crafts alkenylation intermediate. One example is the one-pot synthesis of 2,2-diarylbenzopyrans (**8**) by the reactions of propargyl alcohols (**6**) and phenols (**7**) using TsOH as the catalyst and $(MeO)_3CH$ as the dehydrating agent (Scheme 2).[3] Triarylallene was believed to be the key intermediate, which underwent an electrophilic cyclization to give **8**. Under several Lewis acid catalytic systems, however, the resulted allene intermediate could undergo intramolecular

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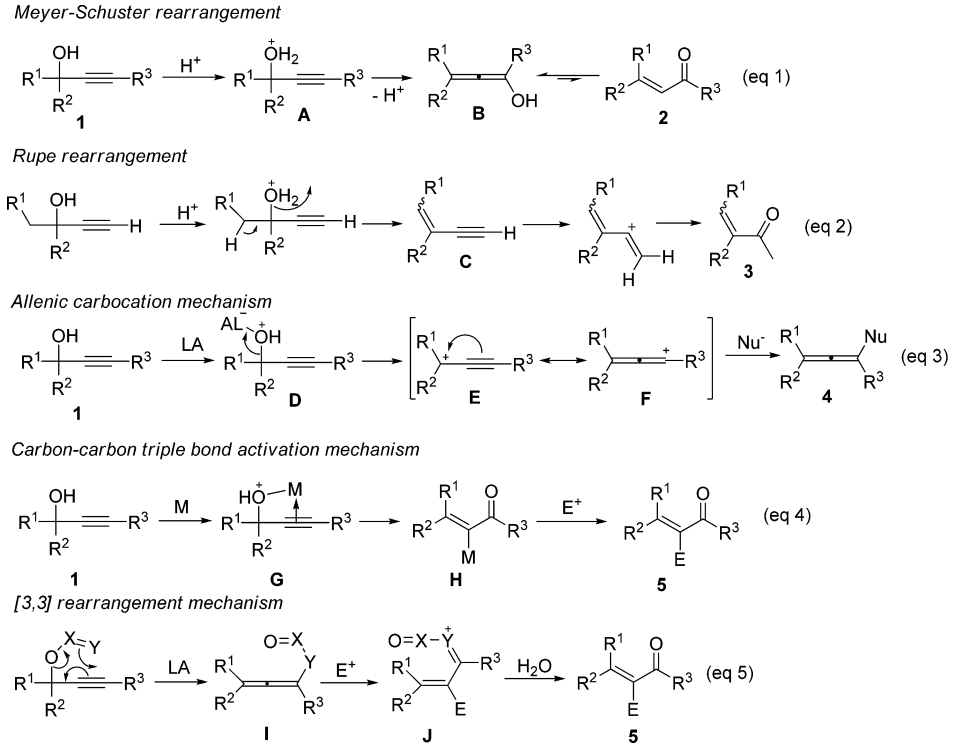
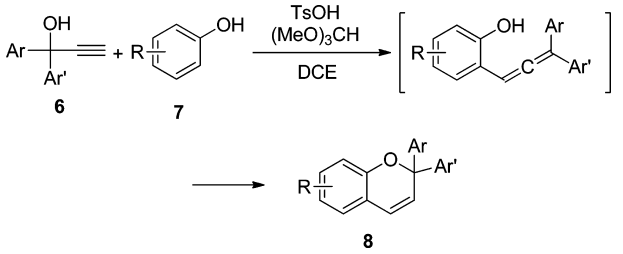
Scheme 1. Meyer−Schuster Rearrangement and Its Alternations

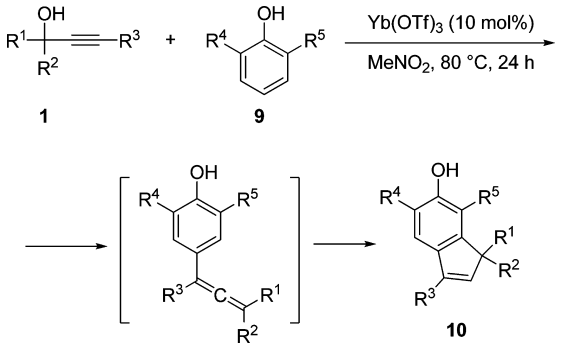


Scheme 2. Preparation of 2,2-Diarylbenzopyrans (8)

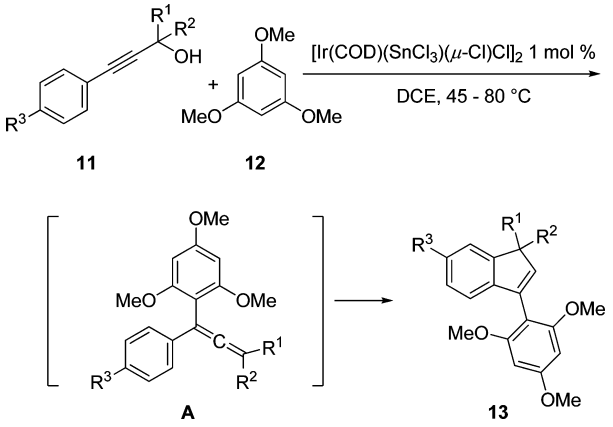


Friedel−Crafts to form indenes as the major products. For example, the $Yb(OTf)_3$-catalyzed reaction of propargylic alcohols **1** with phenols (**9**) led to the synthesis of indenes (**10**) (Scheme 3).[4] A propargylic alcohol rearrangement, an intermolecular Friedel−Crafts alkenylation, and an intramolecular Friedel−Crafts alkylation should be involved in this cascade process. A similar procedure was also developed for the preparation of indenes (**13**) using an iridium complex as a catalyst (Scheme 4).[5] In this case, the allene intermediate **A** was detected by ^1H NMR.

Scheme 3. Ytterbium-Catalyzed Prepartion of Indenes (10)



Scheme 4. Iridium-Catalyzed Preparation of Indenes (13)



Indoles are another class of electron-rich arenes. In 2012, Wang's group reported the reaction of *N*-substituted indoles (**14**) and propargylic alcohols (**15**), which led to a selective synthesis of 3,4-dihydrocyclopenta[*b*]indoles (**16**) and 3-propargylic indoles (**17**) (Scheme 5).[6] The regioselectivity for these transformations, 3-alkenylation or 3-alkylation of indole, could be successfully controlled by applying different catalysts. In the presence of triflic acid, 3-alkenylation of indole occurred and 3,4-dihydrocyclopenta[*b*]indoles (**16**) were constructed via a cascade process. In this case, the rearrangement of propargylic alcohol occurred. Using $Cu(OTf)_2$ as a catalyst, however, the direct alkylation of indoles with propargylic alcohols gave 3-propargylic indoles (**17**). Further treatment with NIS, **17** could be converted to 2-iodo-1,4-dihydrocyclopenta[*b*]indoles (**18**) via the electrophilic cyclization.

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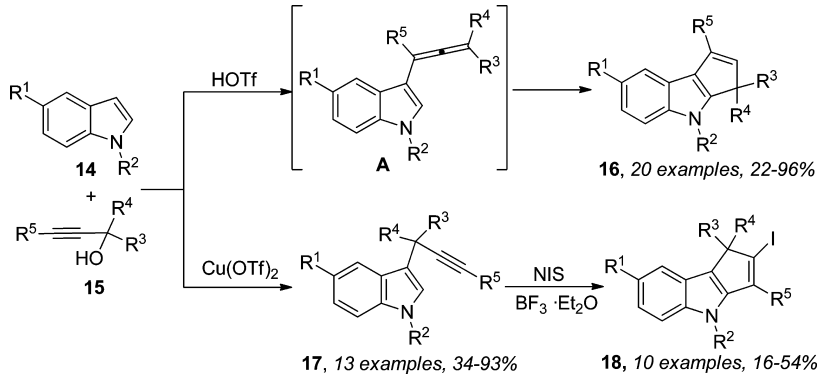
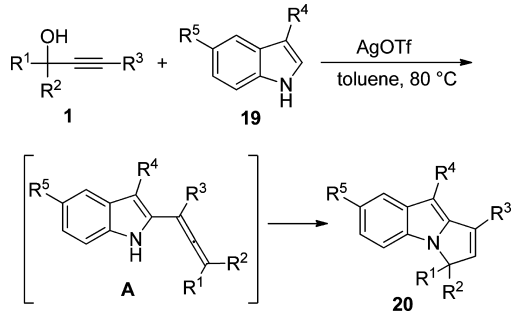
Scheme 5. Catalyst-Controlled 3-Alkenylation or 3-Alkylation of Indoles



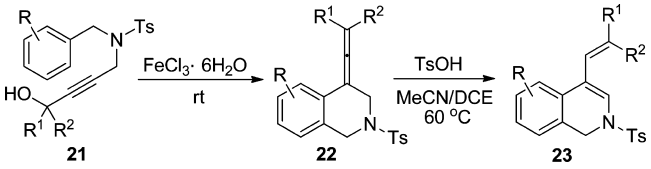
When the 3-position of indole was occupied, the Friedel–Crafts alkenylation occurred at the 2-position of indole. For example, 3-substituted-1H-indoles (**19**) reacted with propargylic alcohols (**1**) in the presence of AgOTf to form 2-alkenylated intermediate **A**, which underwent subsequent cyclization to yield in pyrrolo[1,2-*a*]indoles (**20**) in moderate to good yields (Scheme 6).[7]

Scheme 6. Silver-Catalyzed 2-Alkenylation of 3-Substituted Indoles (19)



When electron-rich arene and propargylic alcohol were embedded in one molecule, an intramolecular Friedel–Crafts alkenylation occurred and substituted tetrahydroisoquinolines (**22**) were prepared with a broad range of substituents (Scheme 7).[8] These compounds could be further converted to

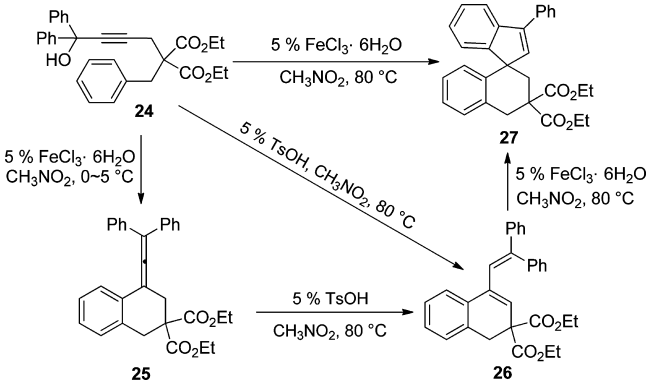
Scheme 7. $FeCl_3$-Catalyzed Cascade Rearrangement of Propargylic Alcohols (21)



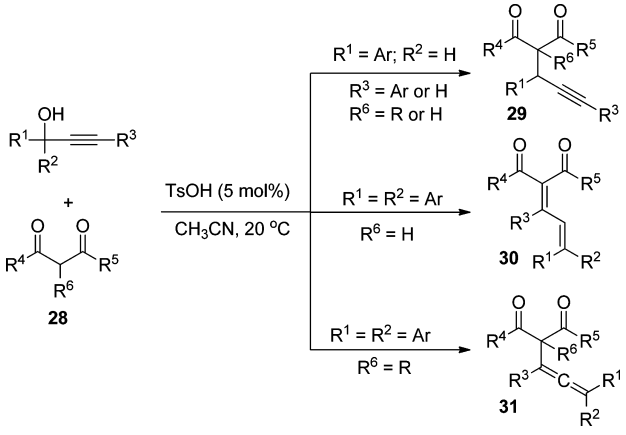
dihydroisoquinolines (**23**) through a 1,3-H shift in the presence of TsOH. Tetrahydronaphthalene (**25**), dihydronaphthalene (**26**), and spirocycle (**27**) were selectively obtained by fine-tuning the reaction conditions from the functionalized propargylic alcohols (**24**) (Scheme 8).[9]

2.2. Trapping Allenic Carbocation with Enols or Enamines. As good nucleophiles, enols and enamines could also react with the reactive allenic carbocation. In 2007, Sanz and co-workers reported a regioselective alkylation and alkenylation of 1,3-dicarbonyl compounds (**28**) with propargylic alcohols in

Scheme 8. Selective Formation of (25), (26), and (27)



Scheme 9. Selective Alkylation and Alkenylation of 1,3-Dicarbonyl Compounds



the presence of TsOH (Scheme 9).[10] The selectivity of this reaction was dependent on the nature of the propargylic alcohols. When one of R^1 and R^2 is aryl and the other is hydrogen, a direct propargylation occurred no matter what R^3 is aryl or hydrogen. In these cases, the rearrangement of propargylic carbocation to allenic carbocation was unfavorable and reaction afforded *α*-propargylated 1,3-dicarbonyl products (**29**) in yields that varied from 43% to 93% with a wide range of substituents. When both R^1 and R^2 are aryl, the rearrangement of propargylic carbocation to allenic carbocation is favorable and the reaction products were dependent on the type of R^6. When R^6 is H, the activated methylene in 1,3-dicarbonyl would react with the *in situ*-formed *α,β*-unsaturated ketone, which was derived from

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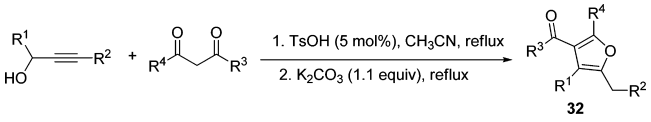
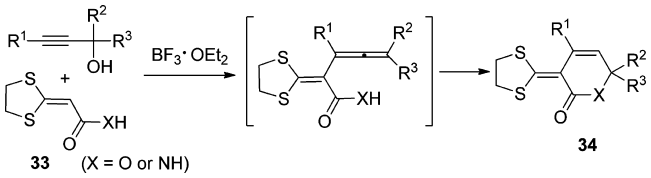
propargylic alcohols through the classic Meyer−Schuster rearrangement. Thus, the conjugated diene-diones (**30**) were obtained in yields between 51% and 83%. In cases of R^6 = alkyl, the allenic carbocation was trapped by the 1,3-dicarbonyl substrates. α-Allenated 1,3-dicarbonyl products (**31**) were prepared in yields between 50% and 72%. Further research indicated that α-propargylated 1,3-dicarbonyl products (**29**) could be used to construct functionalized furans (**32**) in the presence of a base. Without the isolation of the reaction intermediate, a straightforward one-pot process was developed (Scheme 10).

Scheme 10. A Straightforward Method Leading to Trisubstituted Furans



In comparison with enol, the electron-rich vinyl thioether can also function as carbon nucleophile. A more recent example is the Lewis acid-catalyzed reaction of tertiary propargylic alcohols with **33** (Scheme 11).[11] 2-(1,3-Dithiolan-2-ylidene)acetamide

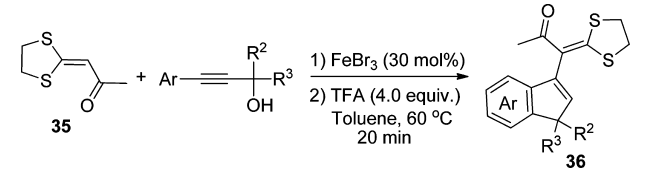
Scheme 11. Synthesis of δ-Lactams and δ-Lactones (30)



(**33**, X = NH) furnished δ-lactams (**34**, X = NH), while 2-(1,3-dithiolan-2-ylidene)acetic acid (**33**, X = O) afforded δ-lactones (**34**, X = O), accordingly. Reactions proceeded via the capture of allenic carbocation by α-oxo ketene dithioacetals and a sequential regiospecific 6-endoannulation.

It is interesting to note that indenes (**36**) could be prepared in yields that varied from 61% to 78% when 1-(1,3-dithiolan-2-ylidene)propan-2-one (**35**) was used as the nucleophile (see Scheme 12). It indicated that the trapping of allenic carbocation by vinyl thioether occurred. The subsequent intramolecular Friedel−Crafts alkylation provided indenes successfully.

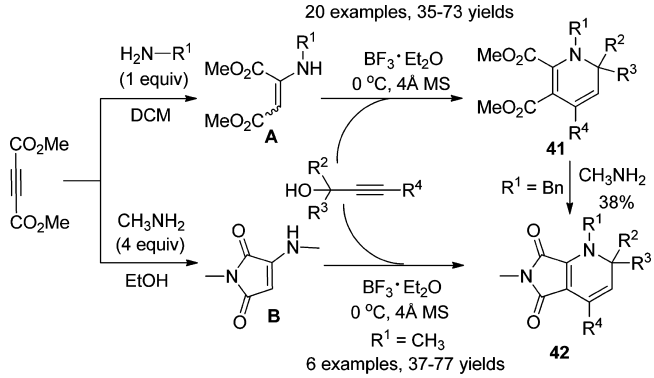
Scheme 12. Synthesis of Indenes (36)



Similar to vinyl thioether, enamine is an alternative source of carbon nucleophile. In 2011, Wang's group developed a three-component approach to afford the highly functionalized dihydroazepines (**40**) from readily available 2-butynedioates (**37**), secondary amines (**38**), and propargylic alcohols (**39**) (Scheme 13).[12] In these cases, the enamine **A**, generated *in situ* from butynedioate and amine, reacted with the allenic carbocation intermediate. A following cascade process afforded dihydroazepines (**40**). Rearrangement of propargylic alcohols occurred and the resulting allenic carbocation was successfully trapped by enamine. A variety of functionalized dihydroazepines **40** were prepared in yields that varied from 40% to 86%.

When a primary amine was used instead of a secondary amine, 1,2-dihydropyridine-5,6-dicarboxylates (**41**) were efficiently constructed through a Lewis acid-catalyzed cascade reaction under mild reaction conditions (Scheme 14).[13] As exceptional,

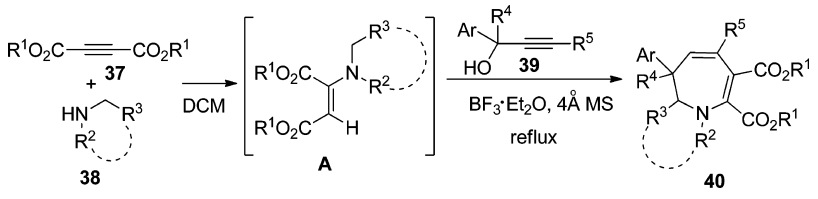
Scheme 14. Cascade Synthesis of 1,2-Dihydropyridines



1*H*-pyrrolo[3,4-*b*]pyridine-5,7(2*H*,6*H*)-diones (**42**) were approached when the primary amine was methylamine. For the formation of **41**, a possible mechanism was proposed as shown in Scheme 15. The enamine captured the *in situ*-generated allenic carbocation (**A**), followed by deprotonation to form 1,3,4-pentatrien-1-amines (**C**). Then, **C** underwent an electrophilic cyclization to afford dihydropyridines (**41**). In cases of methylamine, 1-methyl-3-(methylamino)-1H-pyrrole-2,5-dione was formed and could be isolated. It provides 1*H*-pyrrolo[3,4-*b*]-pyridine-5,7(2*H*,6*H*)-diones (**42**) ideally.

2.3. Trapping Allenic Carbocation with Alkenes. Nucleophilicity of the simple olefin is not strong enough to trap the allenic carbocation, but intramolecular reaction could take place if the olefin is added with water. For example, when propargylic alcohols (**43**), in which alkenes and propargylic alcohols were linked with nitrogen or oxygen, were treated with 10 mol % $AgSbF_6$ in wet CH_2Cl_2, allenic carbocation was formed and trapped by the intramolecular C=C double bond. The resulting allenes **A** could be further converted to 1,3-dienes (**44**) via a retro-ene reaction (Scheme 16).[14]

Scheme 13. Cascade Synthesis of Functionalized Dihydroazepines (40)



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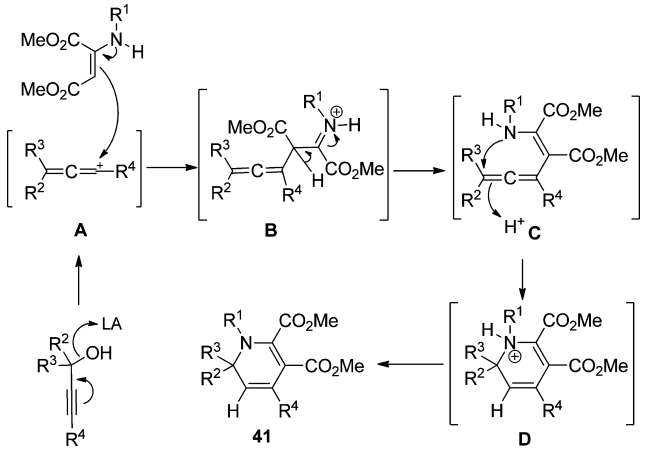
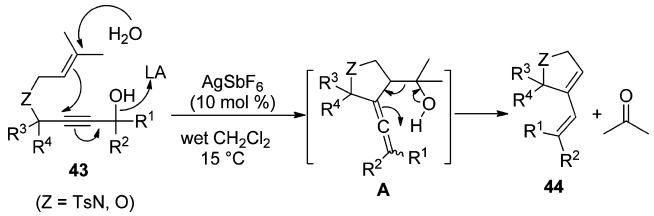
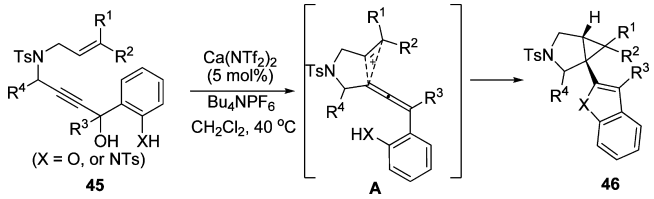
Scheme 15. Possible Mechanism for the Formation of 1,2-Dihydropyridines (41)



Scheme 16. Formation of Dienes (44)



Scheme 17. Synthesis of Fused Heterocycles (46)



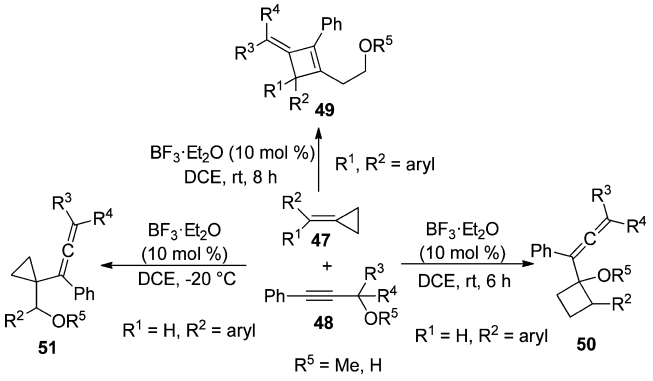
More recently, a similar strategy was applied for the construction of fused heterocycles (**46**) (Scheme 17).[15] A nonclassic carbocation (**A**) was postulated as the key intermediate and executed for the formation of the fused ring.

Methylenecyclopropanes (**47**) are electron-rich compounds and can work as carbon nucleophiles. Shi's group reported that the Lewis acid-catalyzed cascade reaction of methylenecyclopropanes (**47**) with propargylic alcohols or propargyl methyl ethers (**48**) led to the corresponding functionalized methylenecyclobutenes (**49**), cyclobutanes (**50**), or cyclopropanes (**51**) (Scheme 18).[16]

The chemoselectivity of these transformations was well-controlled by the structure of substrates or the reaction conditions. From the proposed mechanisms for the formation of **49**, **50**, and **51** (Scheme 19), it was believed that the reaction selectivity was largely dependent on the stability and the reactivity of intermediate **A**. When both R^1 and R^2 were aryl, cyclization occurred and provided **49**. When one of R^1 and R^2 is hydrogen, ring-expansion occurred at room temperature and furnished **50**. By decreasing the reaction temperature to −20 °C, a direct combination of **A** and anion led to the formation of allenyl cyclopropanes (**51**).

Lately, Shi designed molecule **52**, which combined propargylic alcohol and a methylenecyclopropyl moiety in one molecule. By using an intramolecular rearrangement,

Scheme 18. Cascade Reactions from Methylenecyclopropanes (47)



allenylcyclobutanols (**53**) were obtained with high diastereoselectivities (Scheme 20).[17] Trapping the allenic carbocation, followed by ring expansion, led to the formation of allenylcyclobutanols (**53**). Addition of H_2O favored this cascade rearrangement. The obtained allenylcyclobutanols (**53**) could be stereoselectively converted to a wide range of bicyclic compounds (**54**) via 1,2-R shift. This protocol created a quaternary stereogenic center with a vinyl group substituted.

By using vinylidenecyclopropanes (**55**) instead of methylenecyclopropanes to perform the reaction with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers (**56**), the functionalized 2,4-dihydro-1H-cyclopenta[*b*]naphthalenes (**57**) and 1,2,3,8-tetrahydrocyclopenta[*a*]indenes (**58**) were successfully obtained, depending on the substrates and Lewis acids (Scheme 21).[18] The proposed mechanism was drawn in Scheme 22. At the beginning, propargylic carbocation **A** was formed in the presence of Lewis acid. Vinylidenecyclopropanes (**55**) trapped its resonance structure **B** to form **C**. After cyclization and allylic rearrangement, **E** was generated. When R^3, R^4, R^5, and R^6 were methyls, intramolecular Friedel−Crafts occurred on the phenyl ring of **E**. Thus, 1,2,3,8-tetrahydrocyclopenta[*a*]-indenes (**58**) were obtained. When R^3 and R^4 were aryl, intramolecular Friedel−Crafts occurred on the aromatic part of R^3. In this way, a series of **57** were obtained.

2.4. Trapping Allenic Carbocation with Ylides. In 2009, Wang's group developed a concise synthesis of functionalized indenes (**61**) via a cascade reaction between aziridines (**59**) and propargylic alcohols (**60**) (Scheme 23).[19] In this case, the unusual C−C bond cleavage of aziridine resulted in an azomethineylide **A**. Then, **A** underwent a formal [3 + 2] cycloaddition with allenic carbonation **B**, followed by deprotonation and intramolecular Friedel−Crafts reaction to give indenes (**61**).

2.5. Trapping Allenic Carbocation with Heteroatom Nucleophiles. Both *O*- and *S*- nucleophiles have been indicated to be able to trap the allenic carbocation. Elegant examples include the cascade reaction of propargylic alcohols **1** with thioamides (**61**)[20] and amides (**63**),[21] giving the corresponding functionalized thiazoles (**62**) and oxazoles (**64**) via heteroatom-substituted allene intermediates **A** and **B**, respectively (Scheme 24). Assisted by Brønsted acid, allenic carbocation was generated and trapped by thioamide or amide. A subsequent 5-exo-trig cyclization afforded **62** and **64**. For the formation of oxazoles (**64**), ytterbium triflate was selected as the optimal catalyst. Thiazoles and selenazoles (**67**) were also prepared from the reactions of γ-sulfanyl/selanyl propargylic

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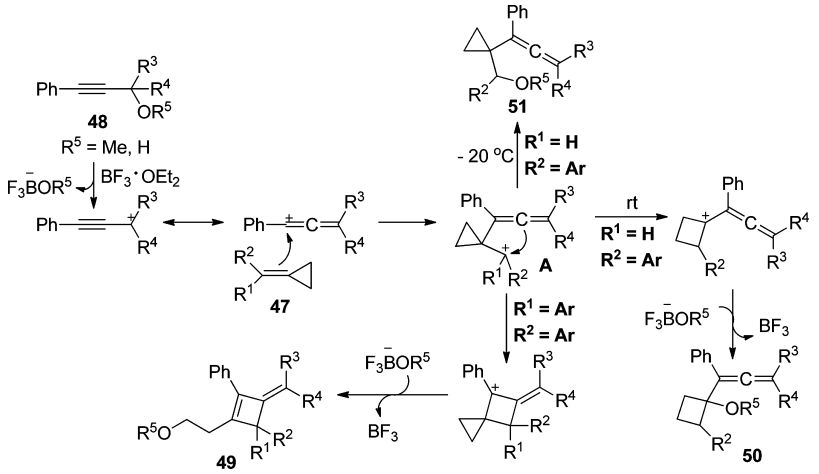
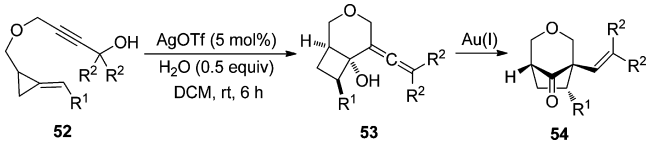
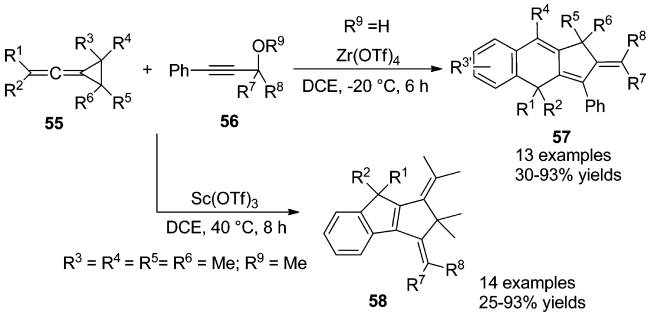
Scheme 19. Proposed Mechanism for the Formation of 49, 50, and 51



Scheme 20. Formation and Conversion of Allenylcyclobutanols (53)



Scheme 21. Cascade Reaction of Vinylidenecyclopropanes (55)

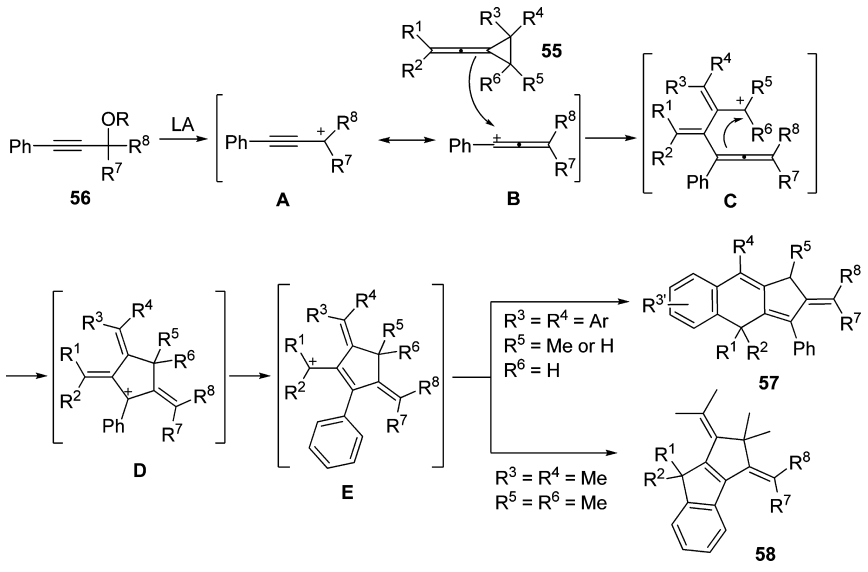


alcohols (**65**) with thioamides and selenamides (**66**), respectively (Scheme 25).[22] In this case, secondary propargylic alcohols could work smoothly using $Sc(OTf)_3$ as catalyst. For the formations of thiazoles (**62**) and oxazoles (**64**), however, only tertiary propargylic alcohols could work well (Scheme 24), while the secondary propargylic alcohols afforded the direct substitution products.

One more example is the Brønsted acid-promoted cyclizations of α-indolyl propargylic alcohols (**68**) with nitrones (**69**). The reaction led to a straightforward synthesis of fully substituted β-carbolines (**70**) (Scheme 26).[23] In this process, the *in situ*-generated allenic carbocation **A** was trapped by nitrone to give intermediate **B**, which underwent a cyclization and resulted in the formation of eight-membered intermediate **C**. Finally, an unusual O-to-C rearrangement occurred and afforded β-carbolines (**70**).

The aza-Meyer−Schuster rearrangement is a process in which the nitrogen atom works as a nucleophile to capture the allenic carbocation intermediate. By employing this strategy, Wang's group successfully synthesized a variety of allenephosphoramides. Thus, in the presence of $Yb(OTf)_3$, triaryl propargyl alcohols (**71**) reacted with diethyl arylphosphoramides (**72**) to

Scheme 22. Mechanism for the Formation of 57 and 58



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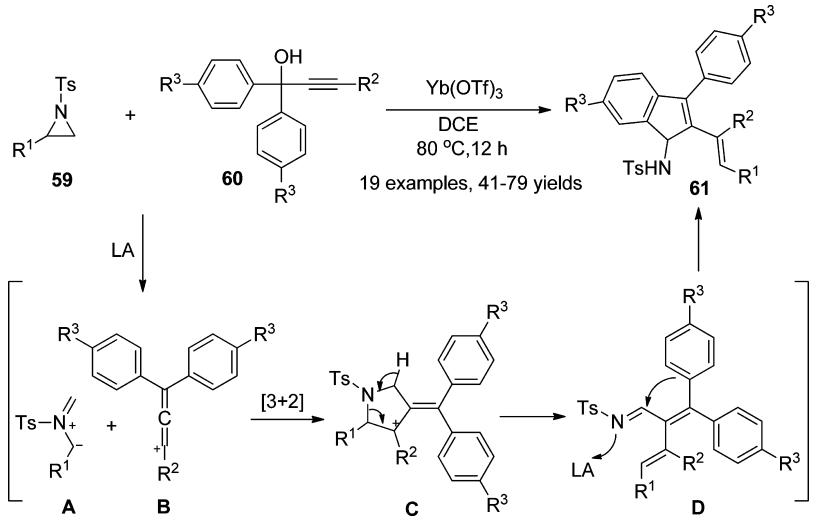
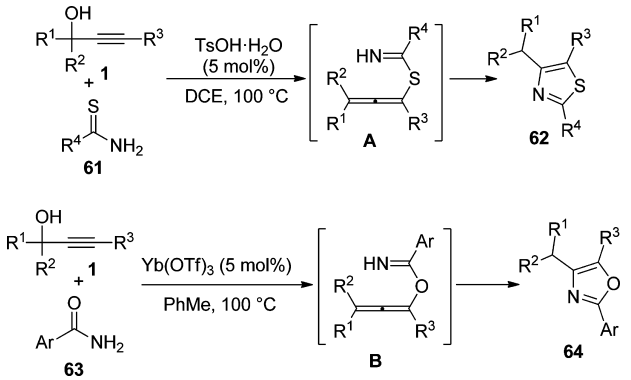
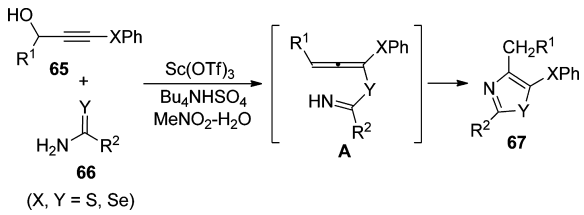
Scheme 23. [3 + 2] Cycloaddition of Ylide with Allenic Carbonation



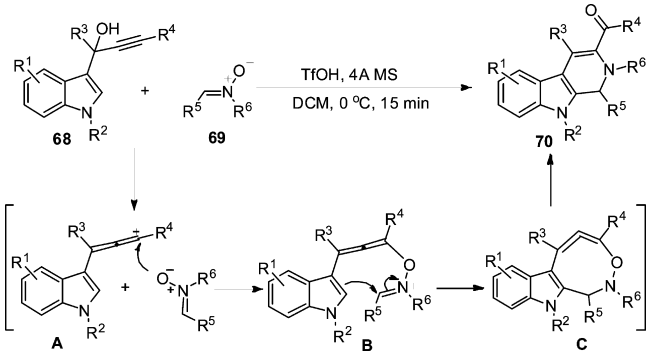
Scheme 24. Cascade Synthesis of Thiazoles and Oxazoles



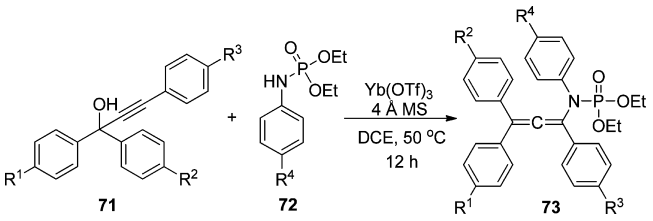
Scheme 25. Cascade Synthesis of Thiazoles and Selenazoles (67)



Scheme 26. Reaction of α-Indolyl Propargylic Alcohols with Nitrones

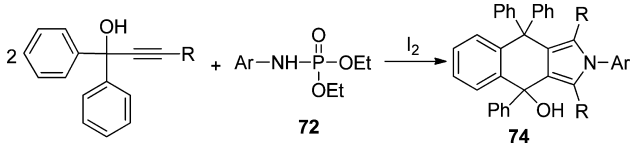


Scheme 27. Preparation of Allenephosphoramides (73)



give allenephosphoramides (**73**) in yields varying from 41% to 84% (Scheme 27).[24] They were stable and could be isolated by column chromatography. The allenamide is a synthetically useful intermediate, because the central carbon of allenamide is electron-rich and can readily react with a variety of electrophiles to construct various heterocycles. For instance, in the presence of I_2, 4,9-dihydro-2*H*-benzo[*f*]isoindole derivatives (**74**) could be efficiently constructed in a single step (Scheme 28). During

Scheme 28. Formation of 4,9-dihydro-2*H*-benzo[*f*]isoindoles (74)



this reaction process, allenephosphoramides **D** was proposed to be the key intermediate (Scheme 29). Further reaction of **D** with iodine successfully afforded 2*H*-benzo[*f*]isoindole derivatives (**74**).

N-Sulfonylallenamines (**A**), which are reactive intermediates, could also be generated from propargylic alcohols (**75**) and sulfonylamides (**76**) via an aza-Meyer–Schuster rearrangement. A subsequent iodination and intramolecular Friedel–Craft alkylation efficiently furnished *N*-(2-haloinden-1-yl) arenesulfonamides (**77**) in moderate to good yields (Scheme 30).[25]

When *N*-sulfonylhydrazones (**78**) and *N*-sulfonyl hydroxylamine (**81**) were used as the nucleophile to trap the allenic carbocation, cyclizations occurred and furnished 4-methylene-1-(phenylsulfonyl)-4,5-dihydro-1*H*-pyrazoles

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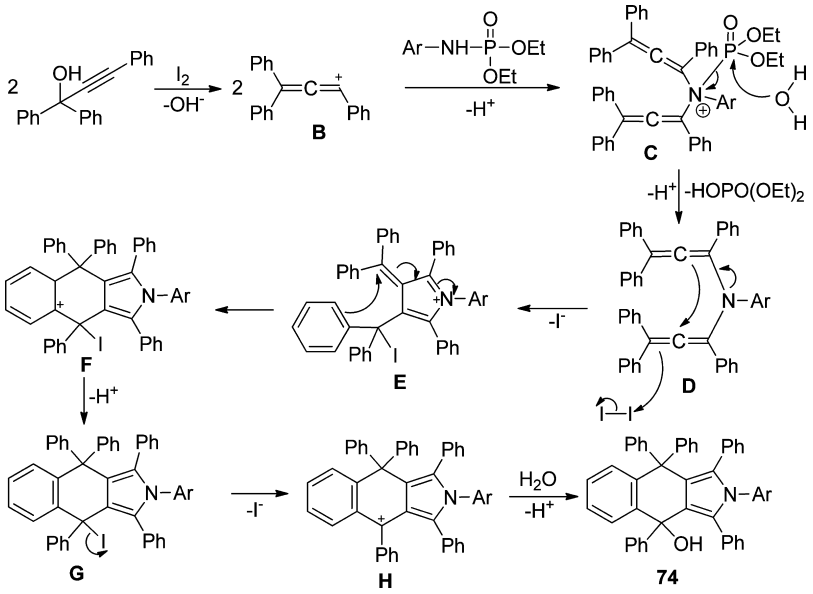
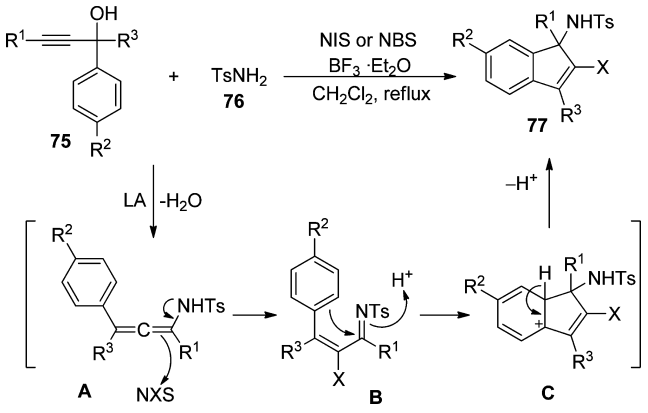
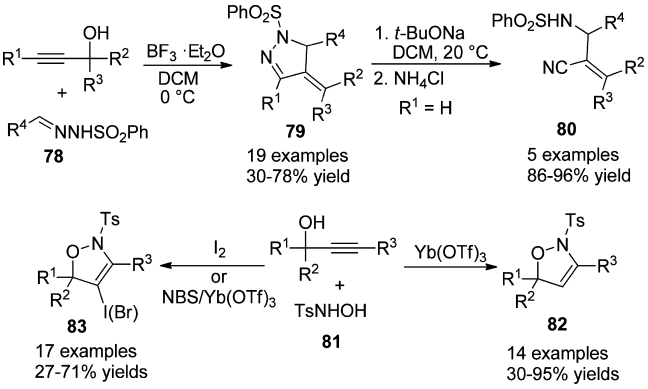
Scheme 29. Possible Mechanism for the Formation of 74



Scheme 30. Formation and Electrophilic Cyclization of *N*-Sulfonylallenamines

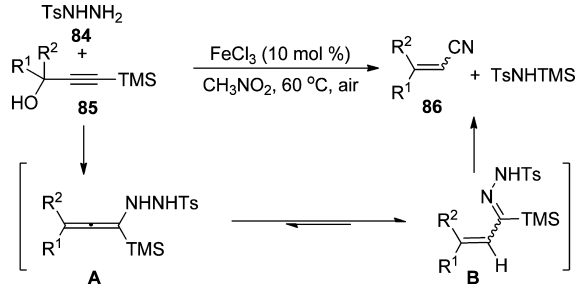


Scheme 31. Cascade Synthesis of 79, 80, 82, and 83



(**79**) and 2,5-dihydroisoxazoles (**82**) (Scheme 31), respectively.[26] In the first case, the resulted pyrazoles (**79**) could be readily converted to 3,3-diarylacrylonitriles (**80**) via E2 elimination using a strong base. In the second case, 4-iodo-2,5-dihydroisoxazoles or 4-bromo-2,5-dihydroisoxazoles (**83**) could be prepared when the reaction was carried out in the presence of iodine or NBS.

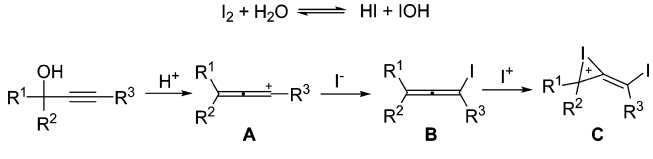
Scheme 32. Formation of Acrylonitriles (86)



Changing *N*-sulfonylhydrazone to sulfonohydrazide (**84**) led to an unprecedented synthesis of acrylonitriles (**86**) (Scheme 32).[27] In the presence of $FeCl_3$, aza-Meyer−Schuster rearrangement occurred. Allenic carbocation was trapped *in situ* by sulfonohydrazide to form **A**. After a sequence of tautoumerism and elimination, acrylonitriles (**86**) were prepared in high yields.

2.6. Trapping Allenic Carbocation with Halide. Allenic carbocation **A** could be formed from propargylic alcohol in the presence of I_2 and H_2O. Because of the existence of iodide in the aqueous iodine solution, **A** could be trapped by iodide to form iodoallene **B**. Further trapping the electron-rich **B** by electron-deficient I^+, which existed in aqueous iodine solution, iodonium **C** could be generated. Both **B** and **C** can undergo a cascade process to approach structurally interesting compounds (Scheme 33). As shown in Scheme 34, the secondary propargylic alcohol (**87**) reacted with aqueous HI to form iodoallene intermediate, which could be further oxidized to α-iodo-α,β-unsaturated aldehydes (**88**) with molecular oxygen in one pot.[28]

Scheme 33. Formation of Iodoallenes and Iodoniums from Propargylic Alcohols



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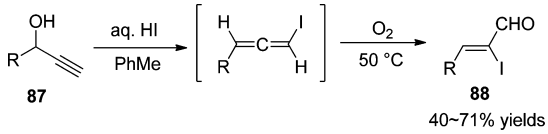
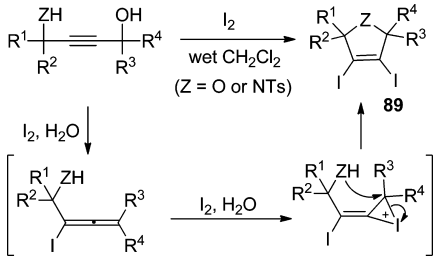
Scheme 34. Preparation of α-Iodo-α,β-unsaturated Aldehydes

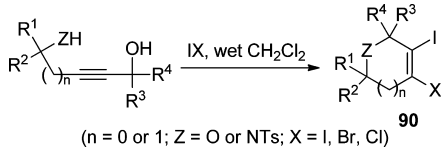


In 2011, Liang and co-workers reported an approach to 3,4-diiodo-2,5-dihydrofurans or 3,4-diiodo-2,5-dihydropyrroles (**89**) via the electrophilic iodocyclization of but-2-yn-1,4-diol or 4-aminobut-2-yn-1-ols through iodoallene and iodonium intermediate (Scheme 35).[29] Lately, this methodology was extended for the synthesis of six-membered heterocyclic compounds **90** (Scheme 36)[30] and 3,4-diiododihydrothiophenes **91**, respectively (Scheme 37).[31]

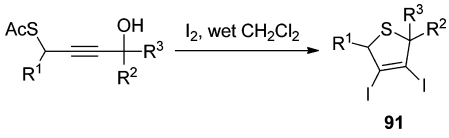
Scheme 35. Preparation of 3,4-Diiodo-2,5-dihydrofurans (89)



Scheme 36. Preparation of 3,3,4-Diiodo-2,5-dihydropyrroles (90)

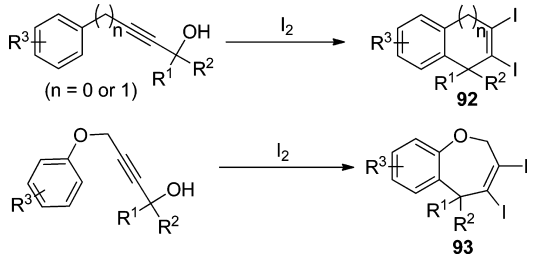


Scheme 37. Preparation of 3,4-Diiododihydrothiophenes (91)



Liang[32] and Wang[33] independently reported a cascade reaction involving the formation of iodoallene and iodonium intermediates, as well as a sequential intramolecular Friedel–Crafts reaction to produce fused rings **92** and **93** (Scheme 38).

Scheme 38. Cascade Approach to 2,3-Diiodoindenes and Its Related Chemistry



The synthesized 1,2-diiodo compounds are useful synthetic intermediates in organic synthesis, especially in the development of conjugated materials. When n = 0, the resulting 2,3-diiodoindenes (**92**) could be further converted to 13*H*-indeno[1,2-*l*]phenanthrenes (**94**) via Suzuki coupling reaction with aryl boronic acid and a sequential Scholl oxidative coupling (Scheme 39). Aromatic hydrocarbons (**94**), with fluorene and phenanthrene subunits, emit blue lights with the quantum yield up to 0.37 and could be used as optoelectronics materials.

A similar example is the electrophilic cyclization of enynes (**95**) (Scheme 40).[34] In this case, the *in situ*-generated iodonium intermediate **A** underwent an electrophilic cyclization to form carbocation **B**, which was subsequently oxidized to 1,2-diiodobenzenes (**96**) with DDQ when R^1 was hydrogen or underwent deprotonation to give diiodocyclohexadienes (**97**) when both R^1 and R^2 were alkyl.

One more interesting example is the electrophilic iodocyclization of 4-hydroxy-2-but-2-yn-1-ones (**98**), which leads to a facile synthesis of 3,4-dihalofurans (**99**) (Scheme 41).[35] MeOH is a crucial solvent for better transformation. As shown in Scheme 42, initial activation of butyone (**98**) with iodine in the presence of MeOH leads to the ketal intermediate **A**. Subsequent dehypoiodination gives allenecation **B**, along with the release of unstable hypoiodous acid (HOI) and iodine anion in the presence of HI. Then, nucleophilic attack of the iodine anion onto the allenic carbocation **B** affords iodoallene **C**, which will react with hypoiodous acid to form iodonium intermediate **D**. Finally, **D** undergoes an intramolecular nucleophilic substitution and elimination to produce 3,4-dihalofurans (**99**).

In 2008, Kim reported a rapid access to 2-iodoindolizinones (**102**) via the 5-endo-dig iodocyclization of propargylic alcohols (**100**), followed by a base-promoted 1,2-R shift (Scheme 43).[36] When the pyridinyl moiety of propargylic alcohols was changed to quinolinyl (**103**), with the decrease in nucleophilicity, pyrrolo[1,2-*a*]quinolines (**104**) were obtained (Scheme 44). It is believed that iodoallene **A** and iodonium **B** are involved as key intermediates in this process.

3. METAL-CATALYZED CASCADE REACTIONS OF PROPARGYLIC ALCOHOLS AND THEIR ESTERS

3.1. Gold-Catalyzed Cascade Rearrangement of Propargylic Alcohols. The classical Meyer–Schuster rearrangement suffers several disadvantages, such as harsh reaction conditions, poor selectivity, limited substrate scope, and the interference of side reactions. For instance, when the propargylic alcohols are activated by Brønsted acid, the Rupe rearrangement cannot be avoided (path a, Scheme 45). Recent investigations demonstrated that activating the carbon–carbon triple bond (C≡C) of propargylic alcohol with a late transition metal, the so-called "soft" Lewis acid, is an effective strategy to exceed these limitations (path b, Scheme 45), although the catalytic mechanism in most cases is not well understood. Gold catalysts have been reported to effective for this purpose.[37]

In 2008, Akai and co-workers demonstrated that the combination of Au and Mo catalysts could accelerate the rearrangement of propargylic alcohols (Scheme 46).[38] Lately, Zhang's group reported the Au/Mo co-catalyzed rearrangement of propargylic alcohols in the presence of electrophiles NIS and NBS, leading to the synthesis of α-iodo/bromo-α,β-unsaturated aldehydes/ketones **105** (Scheme 47).[39] It is believed that the combinatorial catalysis includes the formation of molybdenum

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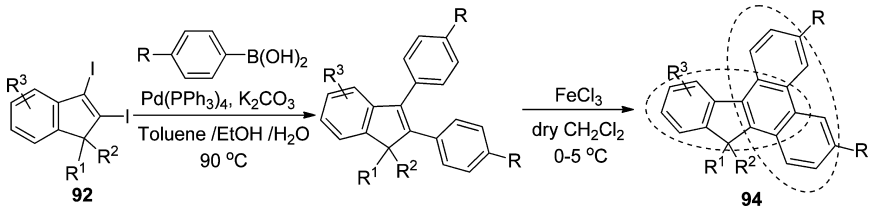
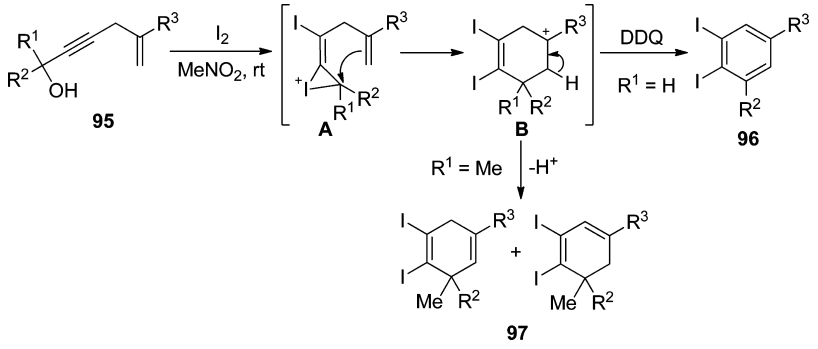
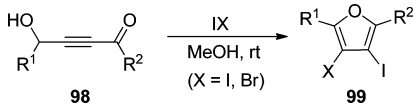
Scheme 39. Synthesis of Aromatic Hydrocarbons (94)



Scheme 40. Proposed Mechanism via Iodonium



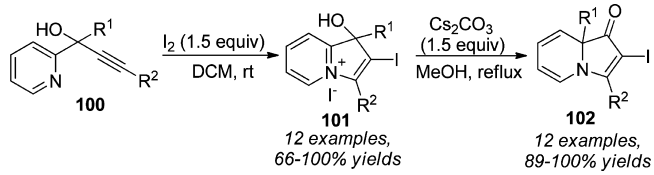
Scheme 41. Preparation of 3,4-Dihalofurans (99)



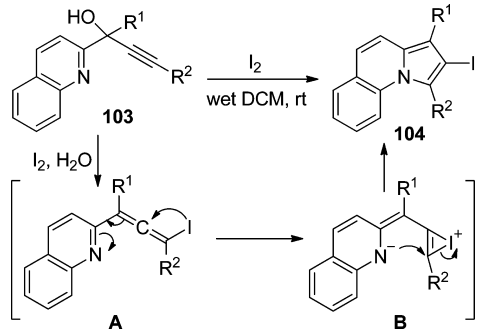
complex **A**, the Au(I)-catalyzed triple bond activation (**B**), and the electrophilic halogenation of enolate **C**.

3.2. Vanadium-Catalyzed Cascade Rearrangement of Propargylic Alcohols. Simple addition reactions and prototropic rearrangements are two major types of atom-economical processes. The combination of Meyer−Schuster rearrangement with aldol- or Mannich-type addition in a single step should be a powerful strategy. Employing tris(triarylsilyl)-vanadate as catalyst, Trost's group successfully accomplished this cascade process. Elegant examples consist of the cascade additions of propargyl alcohols (**106**) with aldehydes (**107**)[40]or imines (**108**),[41] providing the corresponding Aldol-type products (**109**) and 2-acylallylic carbamates (**110**), respectively (Scheme 48). The cascade process is initiated by the transesterification of propargylic alcohols with tris(triarylsilyl) vanadate catalyst. Then, the resulting vanadium propargylic alkoxide **A** undergoes a 1,3-shift to form the allenylvanadium enolate intermediate **B** via a dissociative mechanism.[42] Subsequently, the nucleophilic addition of enolate **B** onto C═O or C═N bond gives the aldol or Mannich adducts, respectively.

Scheme 43. Preparation of 2-Iodoindolizinones (102)

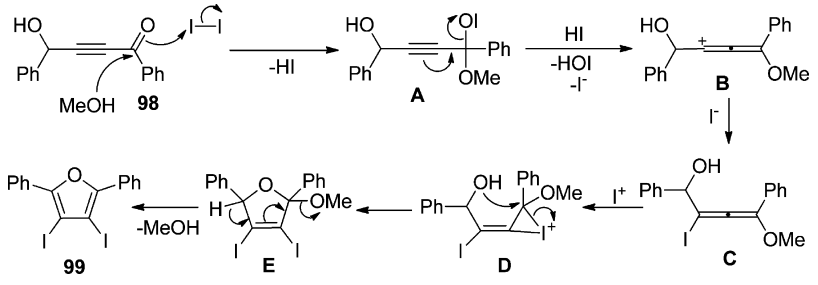


Scheme 44. Formation of Pyrrolo[1,2-*a*]quinolines



It was suggested that the transesterification is the rate-determining step for the oxovanadium-catalyzed Meyer−Schuster rearrangement. For the addition to aldehyde, therefore, electron-rich propargyl alcohols provided aldol-type addition product in

Scheme 42. Proposed Mechanism for the Formation of 99



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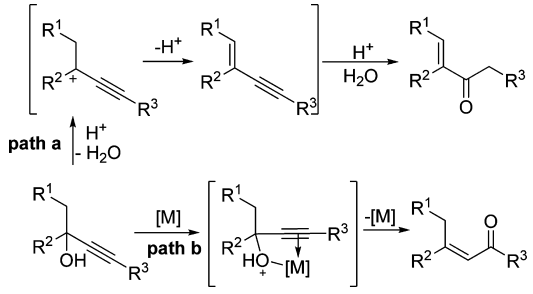
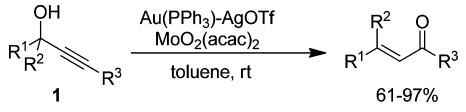
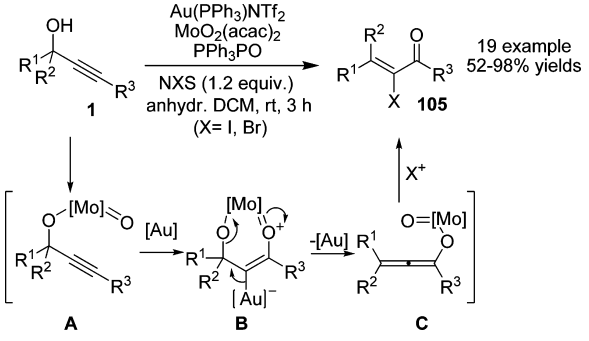
Scheme 45. Comparison of Rupe Rearrangement and Soft Lewis Acid-Catalyzed Meyer−Schuster Rearrangement



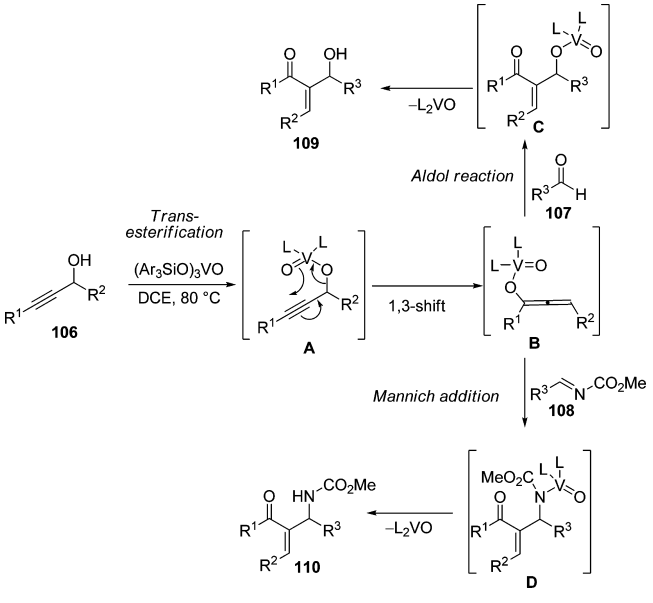
Scheme 46. Au/Mo-Catalyzed Meyer−Schuster Rearrangement



Scheme 47. Au/Mo-Catalyzed Meyer−Schuster Rearrangement in the Presence of X^+



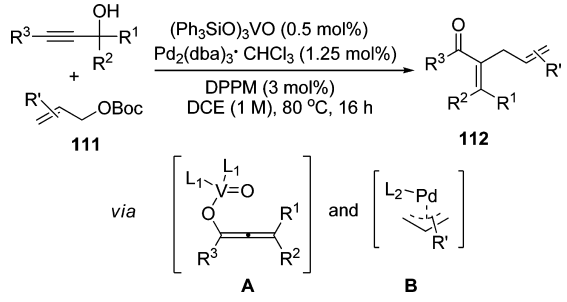
Scheme 48. Vanadium-Catalyzed Addition of Propargylic Alcohols and Aldehydes or Imines



higher yield than the electron-poor propargyl alcohols did. For the addition to imine, *N*-methoxycarbonylimine gave the desired Mannich addition product. Some readily accessible imines, such as *N*-phenyl, *N*-sulfonyl, *N*-phosphorylimines, and *O*-methyl benzyloxime, were disappointing, providing the Meyer−Schuster rearrangement product only.

In 2011, Trost developed a dual catalytic system that combined vanadium-catalyzed Meyer−Schuster rearrangement and palladium-catalyzed allylic alkylation together (Scheme 49).[43]

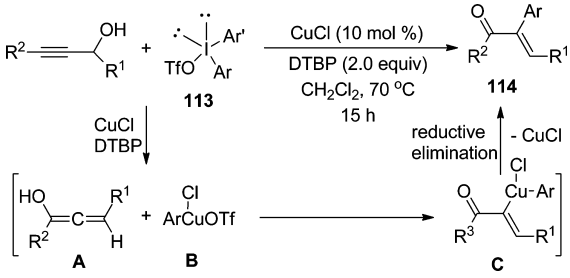
Scheme 49. Cross-Coupling of Vanadium-Allenoate and π-Allylpalladium



Chemoselectivity in this dual catalytic process was successfully achieved by adjusting ligand structure and catalyst ratio of vanadium and palladium catalysts. A range of propargyl alcohols and allyl carbonates (**111**) were readily accommodated in this transformation, which, in turn, provided a novel approach to a variety of α-allyl-α,β -unsaturated ketones, esters, and amides (**112**) in moderate to excellent yields.

3.3. Copper-Catalyzed Arylative Rearrangement of Propargylic Alcohols. The above reactions effectively broadened the utility of the classical Meyer−Schuster rearrangement by using suitable electrophiles instead of the proton to replace the key protonation step in the classic Meyer−Schuster rearrangement. Based on this strategy, various trisubstituted enone products had been obtained under mild reaction conditions in high regioselectivity and stereoselectivity. Moreover, trisubstituted enone products are important synthetic intermediates in modern organic synthesis. Intrigued by these fascinating results, Gaunt practiced the Cu-catalyzed arylative Meyer-Schuster rearrangement by using diaryliodonium salts (**113**) as the electrophiles (Scheme 50).[44] Thus, a

Scheme 50. Cu-Catalyzed Arylative Meyer−Schuster Rearrangement



broad scope of α-aryl-α,β-unsaturated carbonyl compounds (**114**) was prepared in good yields and high selectivity for the *E*-isomer. It is possible that propargylic alcohol undergoes a Cu-mediated 1,3-shift to form the allenol intermediate **A** and Cu(I) is oxidized to Cu(III) species **B** by diaryliodonium salts. Because of the high electrophilicity, **B** is nucleophilically attacked by allenol **A** to form **C**. Finally, **118** is obtained by reductive elimination. Instead of the proton given in the classic

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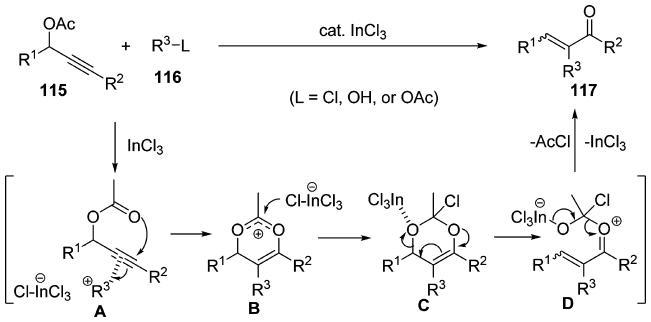
Meyer−Schuster rearrangement, diaryliodonium salts provided the electrophile in this process.

3.4. Indium-Catalyzed Alkylative Rearrangement of Propargylic Acetates. The alkylative rearrangement of propargylic acetates (**115**) has also been achieved using $InCl_3$ as catalyst and alkyl chlorides, alcohols, and acetates (**116**) as electrophiles (Scheme 51).[45] According the mechanism

Scheme 51. Indium-Catalyzed Alkylative Rearrangement of Propargylic Acetates

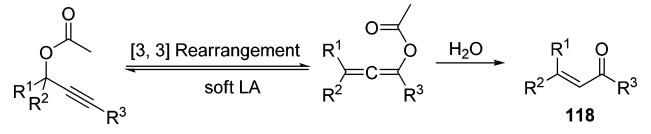


proposed by the authors, $InCl_3$ does not activate propargylic acetates but activates alkyl chloride to generate carbocation **A**, which interacts with propargylic acetate to increase positive charge in the alkyne moiety. Then, the electrophilic addition of carbocation **A** and the nucleophilic addition of the intramolecular acetoxy group to the alkyne moiety occur to give cation intermediate **B**. The addition of a chloride anion to **B** provides **C**. The coordination of the allylic oxygen atom of **C** to $InCl_3$ accelerates the cleavage of C−O bond to give **D**. Then, the elimination of acetyl chloride from **D** affords *α*-alkyl-*α*,*β*-unsaturated carbonyl compounds (**117**).

4. CASCADE REACTIONS OF PROPARGYLIC ESTER VIA [3,3] REARRANGEMENT

The [3,3] rearrangement of the propargylic esters, followed by hydrolysis, could furnish *α*,*β*-unsaturated carbonyl compounds (**118**) (Scheme 52).[46] The advantages of this transformation

Scheme 52. Propargylic Ester via [3,3] Rearrangement

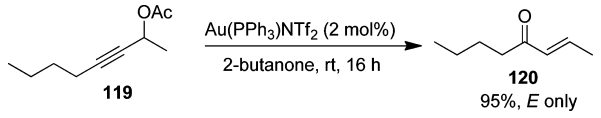


are obvious and include, for instance, low catalyst loading, mild reaction conditions, high stereoselectivity for double bond configuration, and wide substrate scope.

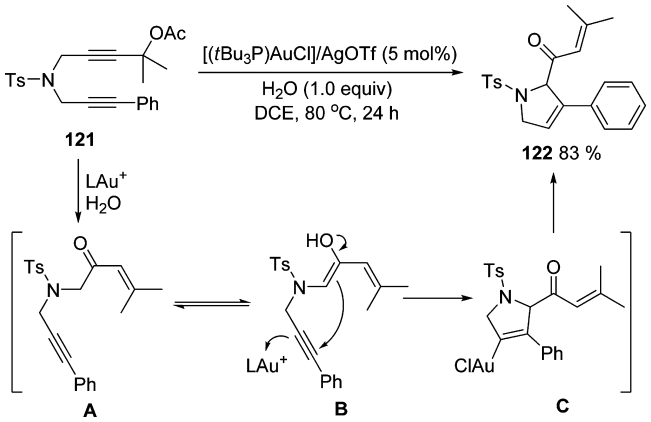
Gold catalysts have been demonstrated to be efficient to promote this transformation. For instance, oct-3-yn-2-yl acetate (**119**) could be converted to (*E*)-oct-2-en-4-one (**120**) with 95% yield, using 2 mol % $Au(PPh_3)NTf_2$ as the catalyst (Scheme 53).[47] This method is general and afforded *β*-monosubstituted enones with excellent *E*-selectivity. Acetates derived from secondary propargylic alcohols work well. For the substrates derived from tertiary propargylic alcohols, the formation of enyne side-products could be avoided by using acetonitrile−water (80:1) as the solvent.

When the substrates contain 1,6-diyne structure in which a nitrogen atom connects two proargylic groups, a cascade reaction would occur in the presence of gold catalyst (Scheme 54).[48]

Scheme 53. Au-Catalyzed Formation of *α*,*β*-Unsaturated Ketones



Scheme 54. Tandem Process to Dihydropyrrole (122)



On the basis of isotope labeling experiments, a possible mechanism was proposed by the authors. They indicated that the propargylic ester (**121**) first underwent a [3,3]-sigmatropic rearrangement, followed by hydration in the presence of gold catalyst to afford *α*,*β*-unsaturated ketone (**A**). Subsequently, ketone tautoumerized to enol **B**, which functioned as a nucleophile and intramolecularly attacked the gold-activated, electron-deficient triple bond. Finally, dihydropyrrole ring was effectively constructed by metal−hydrogen exchange. As they disclosed in the article, 19 examples were given with the highest yield of 88%. Moreover, the tosyl group could be easily cleaved by reduction using sodium and naphthalene.

Gold could catalyze the homocoupling of propargylic acetates (**123**) and resulted in the formation of enone dimer (**124**) (Scheme 55).[49] Although the reaction afforded the dimer in 19% yield only, the reaction mechanism proposed by authors was attractive. They proposed that the reaction underwent the gold-catalyzed tandem hydrolysis of propargylic acetate (**123**) to **A** and a subsequent oxidation by Selectfluor from **A** to **B**. Combination of **A** and **B** led to the formation of **C** via transmetallation. **C** underwent reductive elimination to give the homocoupling product **124**. Using arylboronic acids or arylboronates as the external organometallic reagent, the transmetallation between **B** and arylboronic acids or arylboronates, followed by subsequent reductive elimination to afford the cross-coupling product **125** in 72% yield. Thus, gold-catalyzed rearrangements of propargylic acetates companied by arylation were realized and the cascade reactions resulted in *α*-aryl-*α*,*β*-unsaturated carbonyl products in 45%−72% yields.

Zhang's group developed an efficient synthesis of linear *α*-iodoenones (**127**) via the gold-catalyzed [3,3] rearrangement of the propargylic esters (**126**) (Scheme 56).[50] Good to excellent *Z*-selectivity was observed in the cases of acetates derived from secondary propargylic alcohols. Gold catalyst makes the iodination highly regioselective via a vinyl-gold intermediate **B**.

In 2010, Shi and co-workers reported a selective method for the synthesis of *E*-haloenones (**129**) via a cascade [3,3] rearrangement/electrophilic substitution reaction (Scheme 57).[51]

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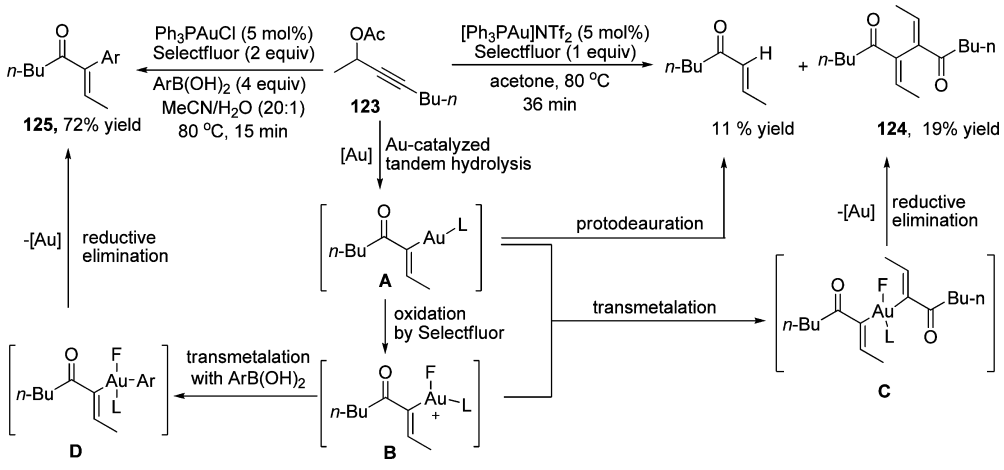
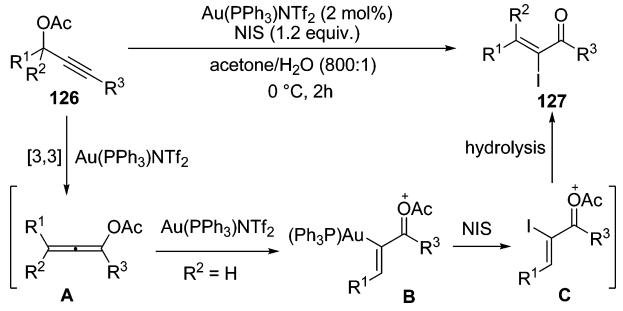
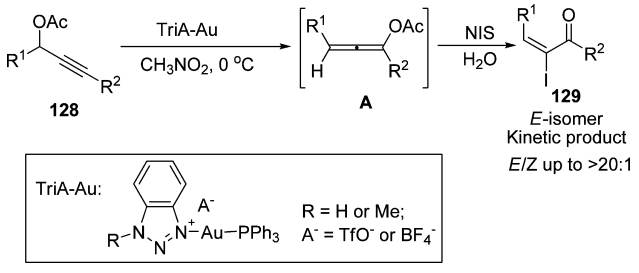
Scheme 55. Homocoupling and Cross-Coupling of Propargylic Acetates



Scheme 56. Gold-Catalyzed Formation of α-Iodo-α,β-unsaturated Ketones

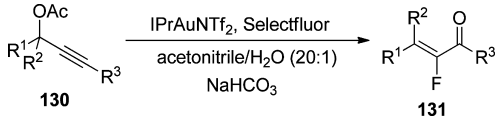


Scheme 57. Gold-Catalyzed Formation of *E*-α-Iodo-α,β-unsaturated Ketones



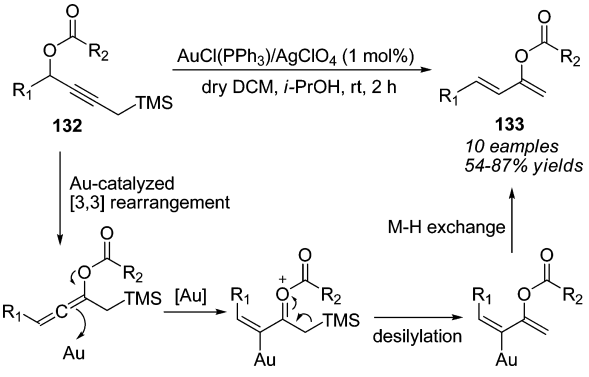
In this case, the triazole-coordinated Au catalyst made the reaction of propargyl acetates (**128**) with NIS generate *E*-α-haloenones. Similarly, in 2011, Nevado's group synthesized α-fluoroenones (**131**) from propargyl acetates (**130**), using $IPrAuNTf_2$ as a catalyst and Selectfluor as an electrophile (Scheme 58).[52]

Scheme 58. Gold-Catalyzed Formation of α-Fluoro-α,β-unsaturated Ketones

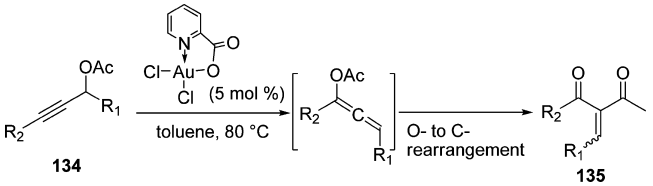


In recent years, Zhang's group developed several cascade reactions involving gold-catalyzed [3,3] rearrangement of propargylic esters, which furnished a wide range of synthetically important compounds, such as alkenyl enol esters (**133**) (Scheme 59),[53] α-ylidene-β-diketones (**135**) (Scheme 60),[54] cyclopentenones (**137**) (Scheme 61),[55] and 1-benzoxyvinyl ketones (**139**) (Scheme 62).[56]

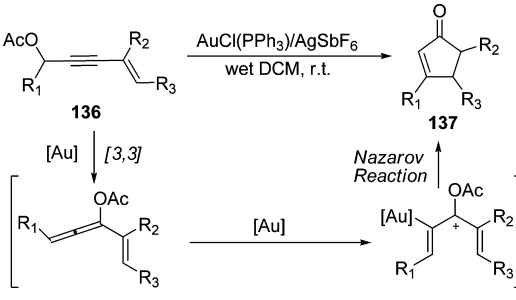
Scheme 59. Gold-Catalyzed Formation of 133



Scheme 60. Gold-Catalyzed Formation of 135



Scheme 61. Gold-Catalyzed Formation of 137



5. CASCADE REACTIONS OF PROPARGYL VINYL ETHER VIA [3,3] REARRANGEMENT

The Claisen rearrangement of propargyl vinyl ether is another important type of rearrangement for propargylic alcohol

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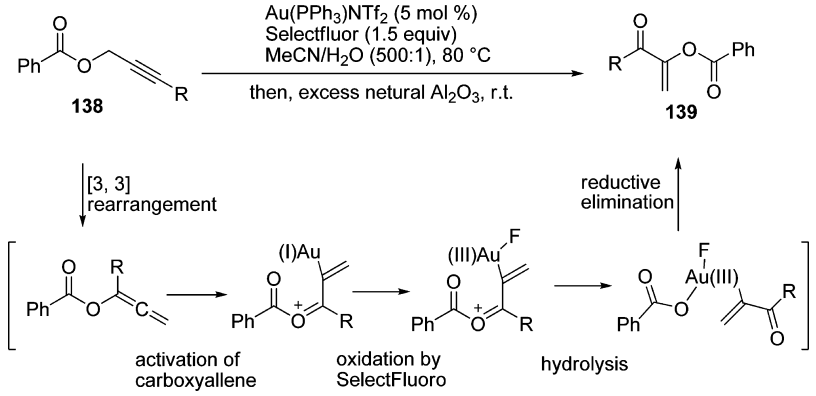
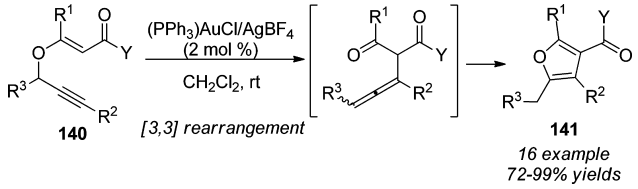
Scheme 62. Gold-Catalyzed Formation of 139



derivatives. One of early examples reported by Kirsch in 2005 is the cascade oxa-Claisen rearrangement/5-*exo-dig* heterocyclization, providing a facile access to tri- and tetra-substituted furans **141** via easily accessible propargyl vinyl ethers **140** (Scheme 63).[57]

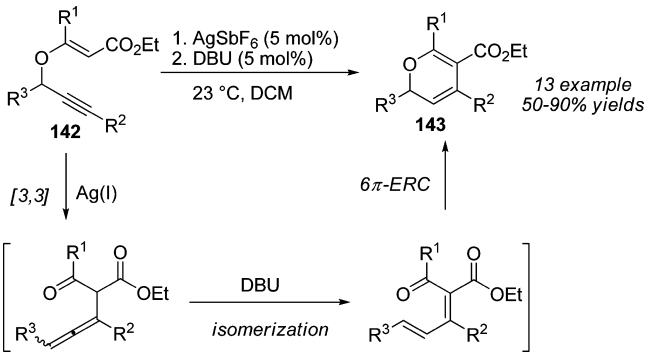
Scheme 63. Gold-Catalyzed Construction of Furans (141)



Cationic triphenylphosphine gold(I) complexes are excellent catalysts for this transformation.

Lately, Kirsch et al. successfully applied propargyl vinyl ethers (**142**) for the synthesis of monocyclic 2*H*-pyrans (**143**) via a Ag(I)-catalyzed oxa-Claisen rearrangement, followed by a base-catalyzed isomerization and 6π-oxa-electrocyclization (Scheme 64).[58]

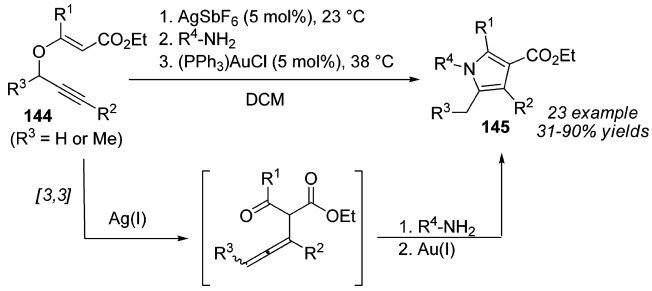
Scheme 64. Ag-Catalyzed Formation of Pyrans (143)



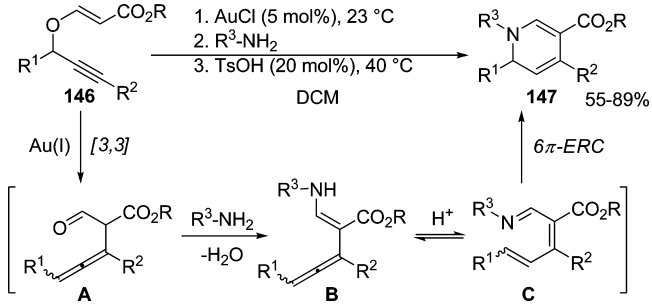
When the base (i.e., DBU) was changed to aromatic amine, the cascade reaction was achieved to furnish pharmaceutically interesting pyrroles (**145**) through a sequence of silver-catalyzed oxa-Claisen rearrangement, an imine formation, and a gold-catalyzed 5-*exo-dig* heterocyclization (Scheme 65).[59]

Recently, Kirsch expanded this chemistry for the one-pot synthesis of 1,2-dihydropyridines (**147**) by changing the catalytic system (Scheme 66).[60] In this case, 5 mol % AuCl was used as catalyst for oxa-Claisen rearrangement and Brønsted acid promoted the heterocyclization. It is believed that enamine **B** is formed via a classical condensation reaction

Scheme 65. Ag-Catalyzed Formation of Pyrroles (145)



Scheme 66. Au-Catalyzed Formation of Dihydropyridines



after oxa-Claisen rearrangement. In the presence of Brønsted acid, the enamine intermediate is further converted to azatriene **C**. Subsequent 6π-electrocyclization furnished 1,2-dihydropyridine (**147**).

6. CONCLUSION

Recent advances in the development of cascade rearrangements of propargylic alcohols have made this class of organic compounds become one of the most useful building blocks available to the synthetic chemist. The Lewis acid-catalyzed cascade rearrangements of propargylic alcohols also have been demonstrated to be an efficient strategy for the construction of carbocycles and heterocycles. The major shortcoming of the classical Meyer−Schuster rearrangement has been surmounted through the use of transition-metal catalysts that coordinate the π-system of the alkyne. The cascade reactions involving [3,3] rearrangement of propargylic esters (both as substrates and as catalytic intermediates) should be a powerful tool for the synthesis of diverse functionalized enones and related compounds. With continuous research in the chemistry of propargylic alcohols and their derivatives, novel reactions and new methods can be

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anticipated to appear in the future and be applied extensively in the practical synthesis.

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Notes

The authors declare no competing financial interest.

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