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Review

The Rearrangement of Alkylallenes to 1,3-Dienes

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Abstract: 1,3-Dienes are vital building blocks in organic synthesis. They underpin many fundamental synthetic transformations and are present in numerous natural products and drug candidate molecules. The rearrangement of an alkylallene to a 1,3-diene is an atom efficient, redox neutral, transformation that provides a straightforward synthetic route to functionalized 1,3-dienes. Herein, we provide an account of this transformation using allenes that are not predisposed by the presence of heteroatoms or electron-withdrawing groups directly attached to the allene. Early reports of this skeletal rearrangement are acid-mediated approaches, with limited substrate scope, but they provide valuable mechanistic insights. More recent transition metal-mediated approaches that exhibit improved substrate scope are described, together with isolated examples that have utilized this rearrangement.

Keywords: allene; rearrangement; 1,3-diene; stereoselective; transition metal

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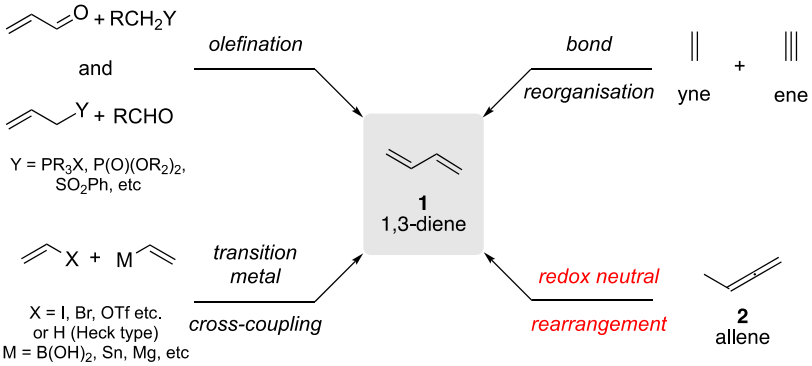
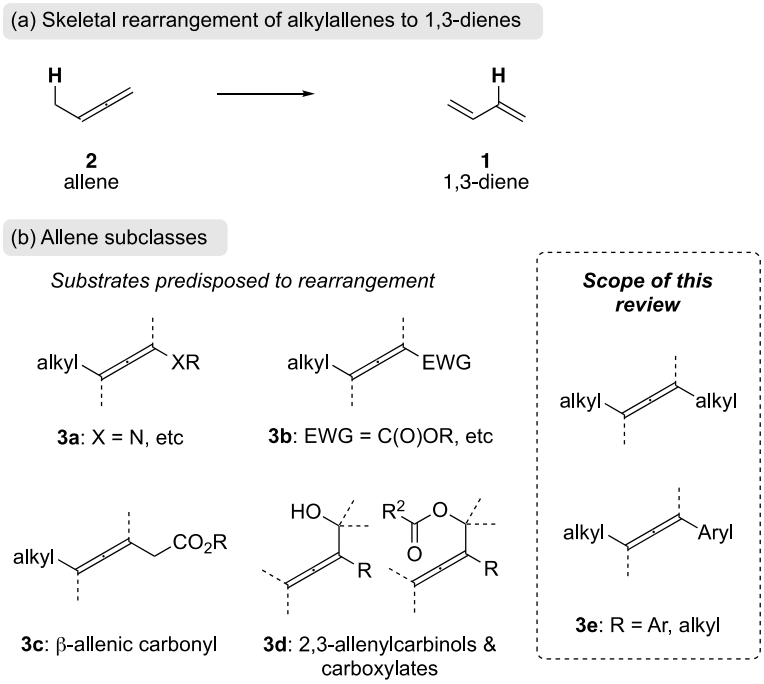
1. Introduction

1,3-Dienes (**1**) are essential building blocks in organic synthesis and materials chemistry. They have been crucial in the development of fundamental synthetic reactions such as the Diels-Alder and related pericyclic transformations [1–5]. The 1,3-diene (**1**) structural motif can be found across numerous natural product classes, as well as in several high-profile on-market drugs and drug candidates; their inherent electronic characteristics have made them indispensable in the development of innovative photoactive organic materials [6–9]. Given their significance, the synthesis of 1,3-dienes (**1**) is rich in history and innovation, and a recent extensive review, centered on stereoselective methods provides an excellent account of current synthetic approaches to the 1,3-diene motif [10]. The application of olefination strategies has dominated their synthesis [11–16]; this was subsequently augmented by transition metal cross-coupling approaches [17–21], and the bond reorganization of appropriately substituted alkene and alkyne substrates [22–25], giving rise to 1,3-dienes (**1**) with unique connectivity's that can be tailored to the synthetic target of choice (Scheme 1).



Scheme 1. Synthesis of 1,3-dienes (**1**).

The rearrangement of an alkyl-allene (**2**) is an appealing approach to the synthesis 1,3-dienes **1,** as it is redox neutral and can be viewed as a formal 1,3-hydrogen migratory process (Scheme 2). Unlike olefination strategies, transition metal cross-coupling, and bond-reorganization approaches, this approach can utilize the inherent thermodynamic stability of the product 1,3-diene to promote the rearrangement.



Scheme 2. (**a**) Rearrangement of an alkylallene to a 1,3-diene. (**b**) Different allene subclasses.

The rearrangement of allenes activated by a heteroatom attached directly to the allene (**3a**) has been reported by Hsung et al. [26,27], and an extensive review has been published by the same authors [28]. An electron-withdrawing group attached directly to the allene will bias it toward rearrangement (e.g., **3b**); this has been realized through phosphine-catalyzed conjugate addition [29–31] and via palladium catalysis [32]. β-Allenic carbonyl substrates (**3c**) are also predisposed to rearrangement, and these substrates can be readily re-conjugated via base catalysis thereby providing dienoic esters, which are present in several natural occurring pheromones and flavors [33–35]. Additionally, while the rearrangement of 2,3-allenylcarbinols and their corresponding carboxylates (e.g., **3d**) can be achieved through a [3,3]-sigmatropic rearrangement [36–38], S_N2' pathways [39–41], and metal-mediated processes [42–44], it does not fall within the scope of this review, as it is not a formal 1,3-hydrogen migratory process. With the emergence of allenes as building blocks in organic synthesis [45,46], the rearrangement of **2** to **1** (Scheme 2) has the potential to be a valuable, complementary tool, in the synthesis of 1,3-dienes. The focus of this review will therefore be the rearrangement of allenes not predisposed to rearrangement through direct attachment of heteroatoms or electron-withdrawing groups (e.g., **3e**).

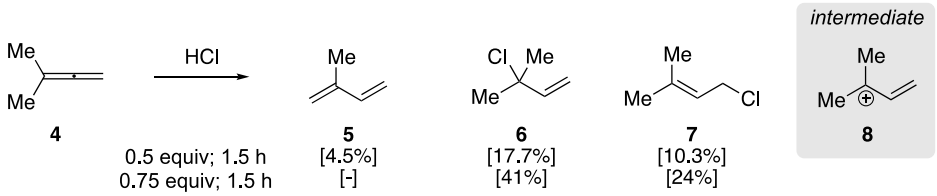
The rearrangement of this allene class has been a focus of interest since the early 1960s, and it is only recently that its synthetic potential has been improved. The review of Soengas and Rodriguez-Solla [10] provides an excellent account of stereoselective methods for 1,3-diene synthesis, and we hope that this review can provide the reader with an appreciation of the origins of the rearrangement and future challenges in improving substrate scope and utility. Therefore, this review begins with an initial account of this rearrangement, centering on thermal and acidic methods. These earlier reports must be examined in context, as they are important in defining scope and generality. Within the literature, isolated examples of this rearrangement have been observed, and frequently, these examples are very substrate specific, or the rearrangement has been observed as a side reaction. Transition-metal-

promoted methods are also analyzed, with the substrate scope being greatly enlarged, thereby providing some of the first synthetically useful methodologies. In this review, the reaction scope for each synthetic approach is highlighted, including substrate bias, the role of electron-rich substituents that may facilitate the rearrangement, and how this impacts the underlying mechanistic rationale for each transformation.

2. Acid-Mediated Rearrangements

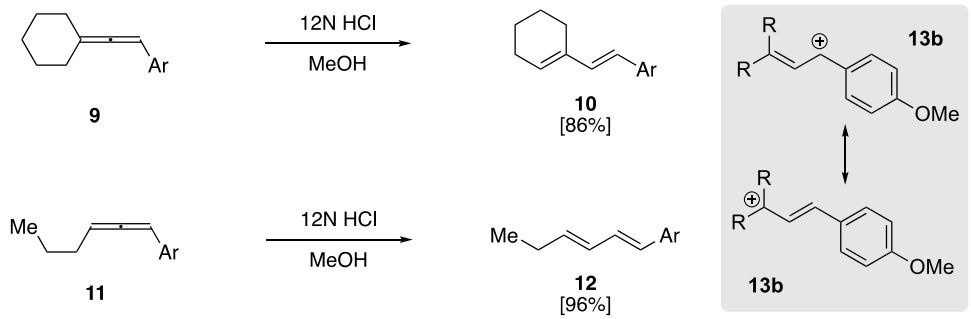
Acid-mediated rearrangements are primarily realized through the protonation of the central sp-hybridized carbon of the allene, where stabilization of a transient carbocation facilitates the formation of a thermodynamically stable 1,3-diene. This method, therefore, limits the scope of the allene substrates that be effectively rearranged to their 1,3-diene counterparts.

In 1960, Johnson et al. examined the addition of hydrogen chloride to aliphatic allenes to elucidate the regiochemistry of the initial protonation [47]. This early report observed the rearrangement of 3-methyl-1,2-butadiene (**4**) to isoprene in the presence of HCl (Scheme 3), clarifying previous studies on the addition of HX to allenes. They found that the treatment of **4** with HCl (0.5 equiv) at −78 °C for 0.5 h yielded a mixture of isoprene **5** and allylic chloride addition products (**6**/**7**), as determined by GC analysis. The ratio of **5** to **6**/**7** could be affected through HCl stoichiometry and reaction time, where an increase in the amount of HCl and reaction time resulted in primarily allylic chlorides **6** and **7**, respectively. The authors rationalized the formation of the products by the protonation of the central sp-hybridized carbon yielding carbocation **8**, with the formation of 1,3-diene **5** resulting from subsequent elimination.



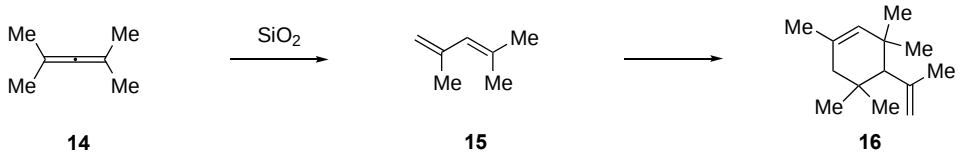
Scheme 3. Acid-catalyzed rearrangement of 3-methyl-1,2-butadiene **4** [47].

Wenkert et al. found that allenes **9** and **11** could be rearranged to 1,3-dienes **10** and **12**, respectively (Scheme 4). [48]. Analogous to the work of Johnson, protonation occurs through the central sp-hybridized allenic carbon to provide an intermediate such as **13**, which can be further stabilized by the electron-donating 4-methoxy aryl substituent. Consequently, both allenes **9** and **11** can be considered as being activated.



Scheme 4. HCl-promoted allene rearrangement. The rearrangement was facilitated by the presence of an electron-rich 4MeO-arene substituent [48].

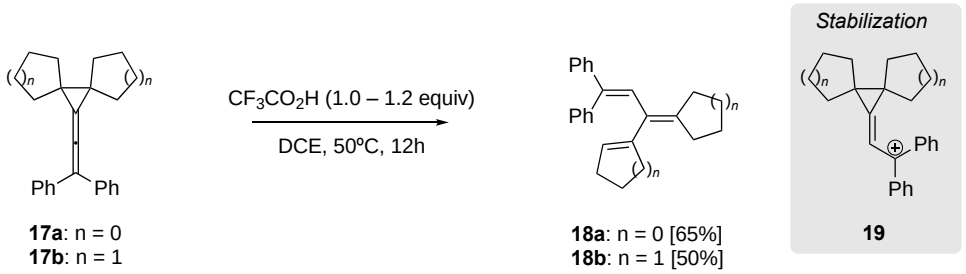
Kropp et al. had demonstrated that silica gel and alumina facilitated the addition of HX to alkenes and alkynes [49]. In a related study, they observed that tetramethylallene **14** could be rearranged to 2,4-dimethylpenta-1,3-diene (**15**) through treatment with silica gel (Scheme 5). However, they found that extended reactions times (24 h) were required to achieve modest conversion and that **15** would undergo further dimerization to produce **16**.



Time	Product (%)		
	14	**15**	**16**
4h	84	16	Trace
24h	52	41	7

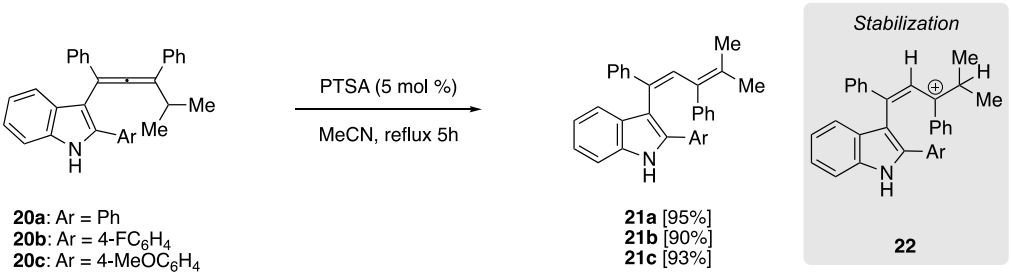
Scheme 5. SiO_2 rearrangement of tetramethylallene **14** [49].

Li et al. utilized the intrinsic strain of diarylvinylidenecyclopropanes in their acid mediate rearrangement to yield trienes (Scheme 6) [50]. For example, the dicyclopentyl (**17a**) and dicyclohexyl (**17b**) diarylvinylidenecyclopropanes could be effectively rearranged to provide trienes **18a** and **18b**, in 65% and 50% isolated yield, respectively. Additionally, using DFT calculations they identified the formation of the carbocation **19** as key within this rearrangement.



Scheme 6. Trifluoroacetic acid-mediated rearrangement of diaryl-vinylidenecyclopropanes [50].

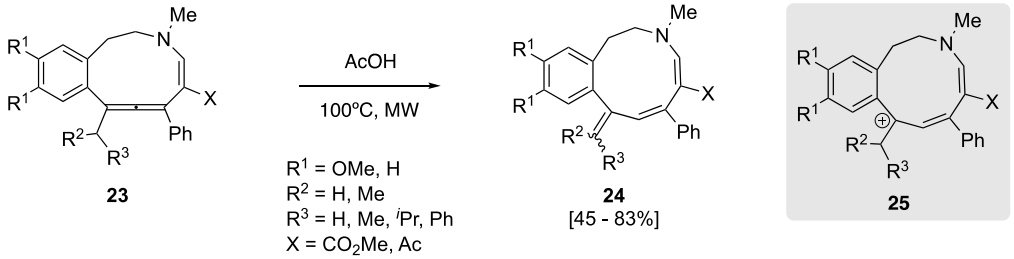
In 2010, Sanz et al. treated indolyl allenes (**20**) in refluxing MeCN and catalytic PTSA, yielding 1,3-dienes **21** in high isolated yield (Scheme 7) [51]. The rearrangement of this allene subgroup benefited from subsequent stabilization of carbocation **22**, formed upon protonation with PTSA. Stabilization is afforded through the participation of electron-rich indolyl substituent, as well as the flanking phenyl groups, although there appears to be no perceived benefit in isolated chemical yield when using electron-poor (**20b,** Ar = 4F-C_6H_4) or electron-rich (**20c,** Ar = 4MeOC_6H_4) aryl substituents.



Scheme 7. PTSA-catalyzed rearrangement of indolylallenes to yield penta-substituted 1,3-dienes. The intermediate tertiary carbocation is stabilized by the electron-rich indolyl substituent [51].

Titov et al., in a study examining the synthesis of potential bioactive tetrahydrobenzazecines, observed that cyclic allene **23** underwent rearrangement to 1,3-diene **24** upon microwave irradiation in acetic acid (Scheme 8) [52]. The yields were found to be good to excellent, depending on the substitution. Again, this type of rearrangement was believed to occur by the benzylic carbocation **25**. This intermediate also benefits from stabilization

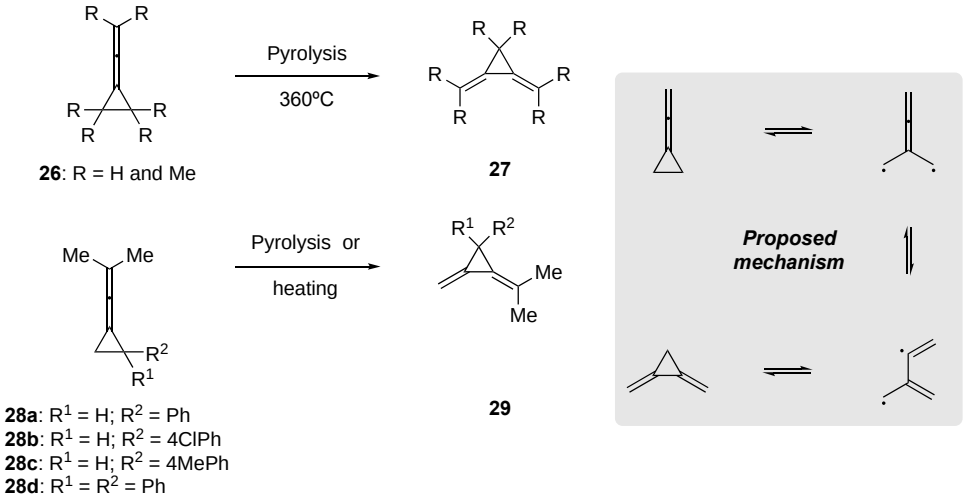
via the *N*-heteroatom of the enamine. Another key driving force for the formation of diene **24**, could well be the release of the inherent ring strain within cyclic allene **23**.



Scheme 8. Acetic acid- and microwave-mediated rearrangement of allenes **23** [52].

3. Thermal-Mediated Rearrangements

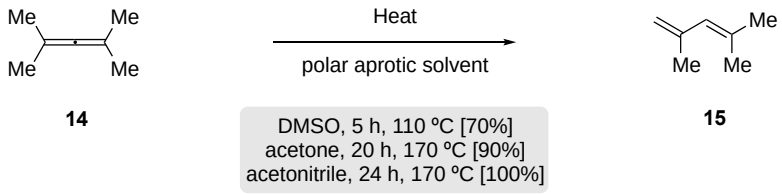
The rearrangement of strained allenic systems, such as the cyclopropyl allenes **26** and **28**, to 1,3-dienes has been known since the late 1960s (Scheme 9). Seminal works by Crandall and Paulson [53], Conia et al. [54], and Maitland Jones et al. [55] demonstrated that thermal rearrangements of strained *exo*-cyclic allenyl cyclopropanes, employing pyrolysis through a flow system at temperatures in excess of 300 °C, gave access to hitherto unknown 1,3-dienyl cyclopropanes through a homolytic ring breakage and subsequent ring-closure events.



Scheme 9. Thermal rearrangement of cyclopropylalkylidenes to cyclopropyl-1,3-dienes [53–55].

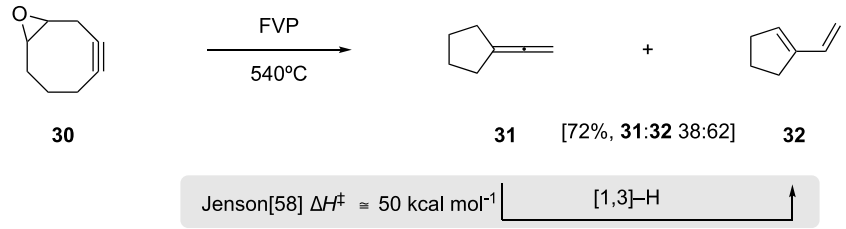
The synthetic utility of this transformation is limited. Rearrangement in these strained allenic systems (e.g., **28a–d**) benefits from aryl substitution on the cyclopropane, and this aligns well with the proposed mechanism to provide added stabilization in the radical process.

In 1968, Taylor and Wright re-examined the thermal rearrangement of tetramethylallene **14**, as prior reports had shown that **14** undergoes dimerization at 150 °C [56]. They observed that heating of **14** in a glass vessel that had been pre-treated with base gave the dimer, tetramethyl-1,2-di-isopropylidenecyclobutane. However, in an unwashed or acid-treated vessel, rapid rearrangement to 1,3-diene, 2,4-dimethylpenta-1,3-diene (**15**) was observed; subsequently, **15** underwent further dimerization to yield a complex mixture. This led to a synthetically useful procedure being established, where the allene **14** could be successfully rearranged to 2,4-dimethylpenta-1,3-diene (**15**) through heating a diluted solution in a polar aprotic solvent at elevated temperatures (Scheme 10).



Scheme 10. Thermal rearrangement of tetramethylallene in polar aprotic solvents [56].

In 1989, Meier and Schmitt observed a formal 1,3-hydrogen shift in the *exo*-cyclic allene **31** (Scheme 11) [57]. Upon Flash Vacuum Pyrolysis of the cyclooctynyl epoxide **30**, they observed two major products in 72% yield, *exo*-cyclic allene **31** and 1,3-diene **32** in a 38:62 ratio. The 1,3-diene was postulated to occur through formal [1,3]-hydrogen migration. Experimentally this reaction occurs at 540 °C under the FVP conditions; Jenson, in a very insightful theoretical study on the effects of allenes in sigmatropic H shift, subsequently calculated an energy barrier of $\Delta H^{\ddagger}$ of ≅50 kcal mol^{-1} for this thermal [1,3]-H rearrangement [58].

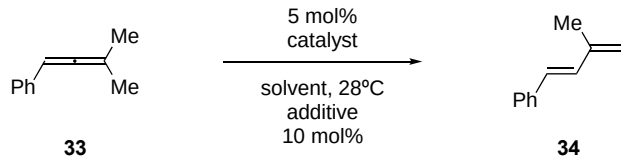


Scheme 11. Flash vacuum pyrolysis of the epoxides provides a mixture of the allene and 1,3-diene [57]. A subsequent theoretical study by Jenson provided an energy barrier for this rearrangement [58].

4. Transition-Metal-Promoted Rearrangements

4.1. Gold

Due to their carbophilic character, gold catalysts are ideal for the selective activation of allenes to nucleophilic attack [59]. An Au(III)-catalyzed rearrangement of aryl-substituted allenes to 1,3-dienes was accomplished by Liu et al. (Scheme 12) [60,61]. This report is important, as it provides a catalytic method to achieve this rearrangement at ambient temperature, and importantly, it exhibited excellent substrate scope.



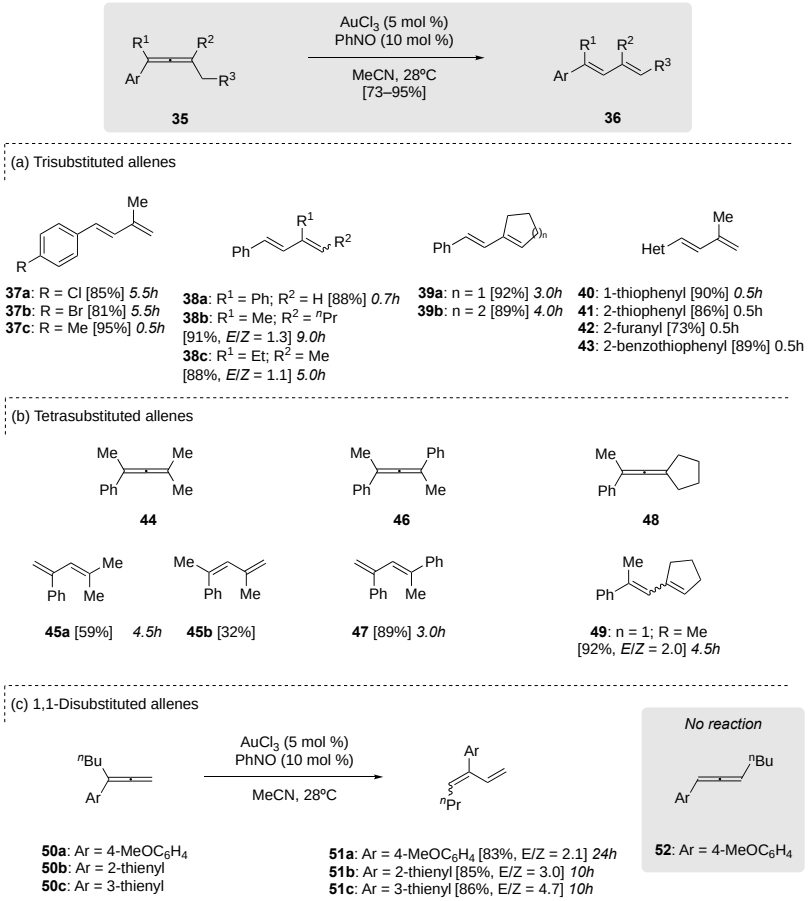
Cat.	Additive	Solvent	Yields (%) 33	34
AuCl	PhNO	CH_2Cl_2	52%	43%
$AuCl_3$	PhNO	CH_2Cl_2	-	92%
$AuCl_3$	DBU	CH_2Cl_2	92%	-
$AuCl_3$	PhNO	CH_3CN	-	91%

Scheme 12. Accomplishing the rearrangement of allenes at ambient temperature through the action of $AuCl_3$ and nitrosobenzene (PHNO) [60].

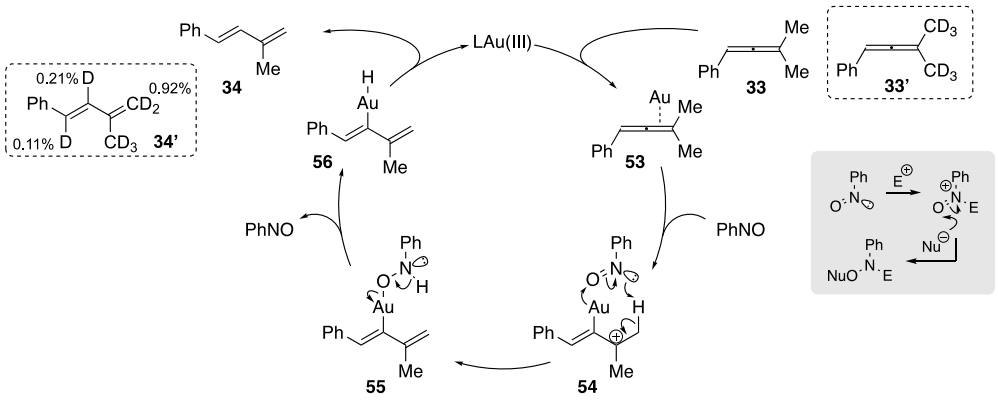
Reaction optimization revealed that $AuCl_3$ (5 mol%) with 10 mol% of PhNO at 28 °C for 2 h, was essential to achieve full rearrangement; Au(I)-catalysts such as AuCl provided only partial 1,3-diene product **34** and reduced chemical yields of **34** were observed when

reaction times were in excess of 2 h. When the additive PhNO was replaced by tertiary amines such as DBU or Et_3N, no rearrangement was observed, and replacing the solvent with CH_3CN or DCE resulted in a marginal reduction in the yield of 34. However, solvents such as 1,4-dioxane or toluene resulted in little-to-no observed 1,3-diene product **34**. The scope of the transformation was examined on di-, tri-, and tetrasubstituted allenes.

For tri- and tetrasubstituted allenes, all reactions were performed with $AuCl_3$ (5 mol%) and PhNO (10 mol%) at 28 °C, but the duration of each was substrate dependent and ranged from 0.5 h to 72 h (Scheme 13). For example, the trisubstituted 1,3-dienes **37a** and **37b** required significantly more time to achieve reaction completion, compared with **37a**. 1,3-Dienes **38b** and **38c** were obtained as mixtures of geometric isomers, with each isomer being isolated as the internal olefin through an extended reaction time of 9 h and 5 h, respectively. Isolated chemical yields were good to excellent, and the double bond geometry of the isolated 1,3-dienes reflected thermodynamic equilibrium; this also accounts for the extended reaction times particularly in the formation of 1,3-dienes **38b** and **38c**, respectively. The isomerization was shown to be applicable to heteroaromatic allenes, providing 1,3-dienes **40**–**43** in very good yields and short reaction times. Tetrasubstituted allenes **44**, **46**, and **48** performed well, providing 1,3-dienes **45**, **47,** and **49**, respectively. In the case of **44**, the product 1,3-dienes were isolated as a mixture of **45a** and **45b** in approximately 2:1 ratio. Under the reaction conditions, 1,1-disubstituted allenes required heating to 50 °C and extended reaction times (Scheme 13c). Under the reactions conditions 1,2-disubstituted allene **52** failed to undergo any rearrangement with only starting material being returned in 43% yield. Significantly, this result implies that the formation of a tertiary carbocation is vital to this Au(III)-catalyzed transformation (see Scheme 14).



Scheme 13. (**a**,**b**) Tri- and tetra-allene reaction scope of Lui's Au(III)/PhNO rearrangement. (**c**) 1,1-Disubstituted allene rearrangement can be accomplished using Au(III)/PhNO protocol; 1,2-disubstituted allenes do not participate. For comparison, the reaction times (h) for each rearrangement are given in italics [60].



Scheme 14. A proposed mechanism for the Au(III)/PhNO-assisted rearrangement [60].

A mechanism for this transformation is presented in Scheme 14. Following allene activation by Au(III), the authors proposed the formation of an initial tertiary carbocation **54.** Nitrosobenzene then facilitates a cooperative intramolecular proton transfer ultimately providing **56** that undergoes protodeauration to yield the observed 1,3-diene (**34**). Importantly, deuterium-labeling experiments using **33′** provided evidence of the mechanism with deuterium incorporation at C_1 (0.11%) and C_2 (0.21%) within **34′**.

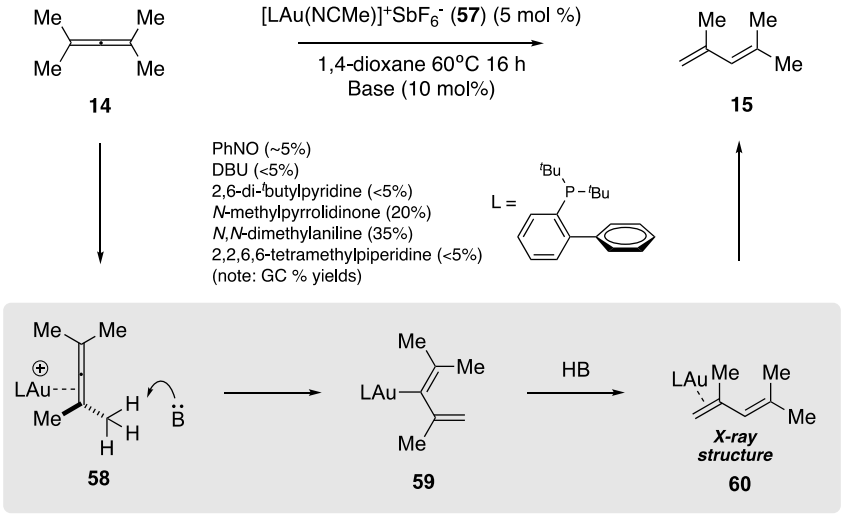
The Au-catalyzed rearrangement described by Lui et al. [60,61] works solely for aryl-substituted allenes. There are limited examples of the rearrangement of alkyl-substituted allenes within the literature. The rearrangement of a cationic tetramethylallene complex Au(I) complex has been established by Widenhoefer et al. (Scheme 15) [62]. Treatment of tetramethylallene (**14**) with Au(I) complex **57** generates the π-tetramethylallene complex **58** in a 96% isolated yield. Attempts at the crystallization of this Au(I) complex led to rearrangement, via a formal 1,3-hydrogen migration, to the π-1,3-diene complex **60**, whose structure was confirmed by X-ray analysis. The authors were able to estimate the enthalpy for the conversion of **58** to **60** to be −8.6 kcal/mol based on the calculated heats of formation and binding affinities of 2,4-dimethyl-2,3-pentadiene (**14**) and 2,4-dimethyl-1,3-pentadiene (**15**), respectively. The authors also probed a deprotonation mechanism to account for the transformation and found that heating a solution of **58** with 1 equiv. of triethylamine yielded approx. 50% rearrangement and quantitative ligand displacement to form a 2:1:1 mixture of **57**. $NEt_3{}^+SbF_6{}^-$, 2,4-dimethyl-2,3-pentadiene (**14**) and 2,4-dimethyl-1,3-pentadiene (**15**). The mechanism of the rearrangement was postulated to occur through deprotonation of the allenylmethyl, providing the Au σ-dienyl intermediate **59** that subsequently underwent protodeauration. This mechanism was reinforced by the work of Das et al., who performed an in-depth DFT study on the Au(III)/PhNO-catalyzed rearrangement of substituted allenes to 1,3-dienes [63]. Attempts by Widenhoefer et al. at improving the efficiency of this rearrangement by using weakly coordinating bases revealed *N*,*N*-dimethylaniline to be the most effective, providing 2,4-dimethyl-1,3-pentadiene (**15**) in an improved 35% GC yield.

As seen above, the rearrangement of an alkyl-substituted allene to a 1,3-diene is still limited in reaction scope. However, the detailed work by Widenhoefer et al. [62], together with computational studies [63], may provide opportunities to expand this scope and complement the methodology reported by Lui et al. [60,61].

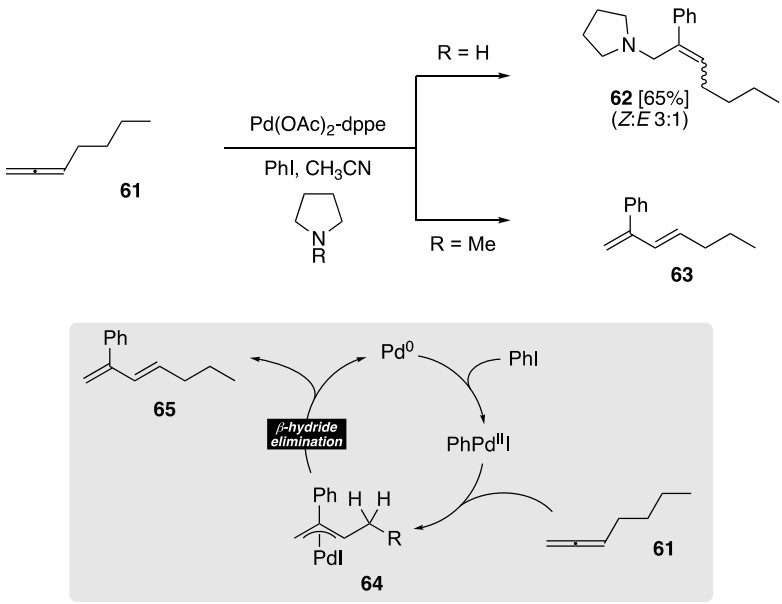
4.2. Palladium

The reaction of Pd(0) with 1,2-dienes has been extensively studied and provides a convenient method to access synthetically useful π-allylpalladium intermediates [64]. Prior to the work of Tsuji et al. [65,66], the fate of this intermediate was oligomerization or polymerization. A key study by Tsuji found that this π-allylpalladium species could be intercepted by secondary amine nucleophiles such as pyrrolidine to generate allylamines (Scheme 16). However, the authors also observed that the π-allylpalladium species derived from 1,2-heptadiene, in the presence of *N*-methylpyrrolidine, generated 1,3-diene **65**,

exclusively. The authors postulated that in the absence of a suitable nucleophile, in this case, *N*-methylpyrrolidine, the intermediate π-allylpalladium species **64** instead undergoes elimination of HPd, yielding the observed 1,3-diene **65**. While this is not formally a direct rearrangement of an allene to a 1,3-diene, given the intermediate π-allylpalladium species **64** is a consequence of the *syn* arylpalladium addition, it does represent the mechanistic basis of subsequent direct allene to 1,3-diene rearrangements via Pd catalysis.

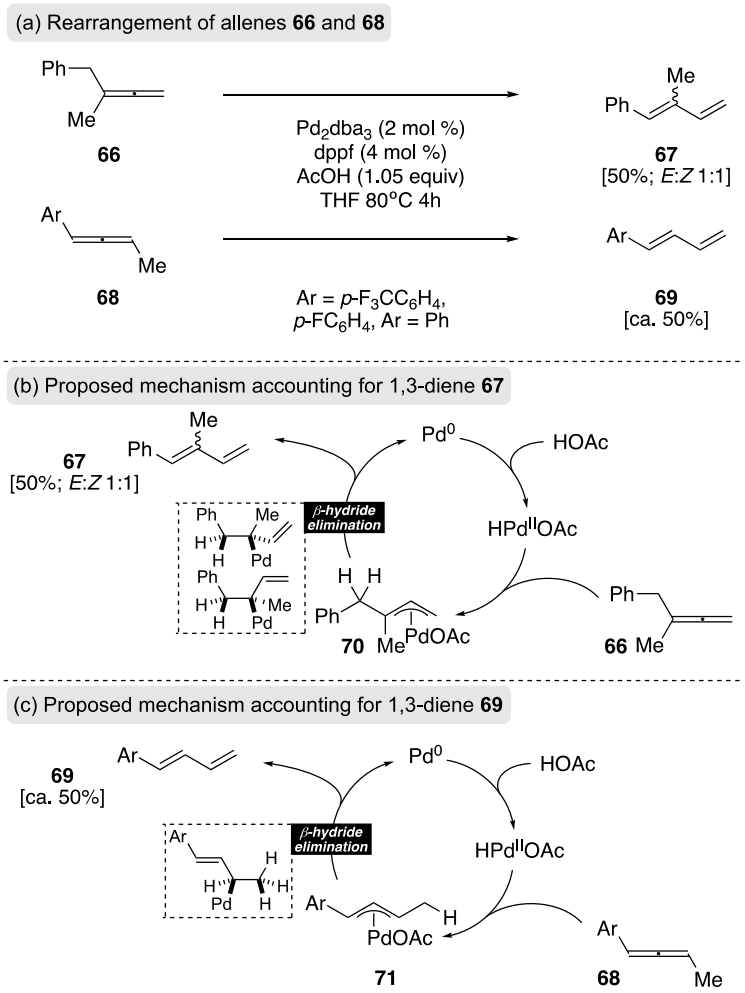


Scheme 15. Widenhoefer's Au(I)-facilitated rearrangement and the effect of different bases on the product outcome [62].



Scheme 16. Early work by Tsuji provided the basis of the β-hydride elimination pathway yielding 1,3-diene **65** [65,66].

The first direct rearrangement of 1,2-diene to 1,3-diene through palladium catalysis was reported by Al-Masum and Yamamoto [67]. Building on previous reports on the addition of nucleophiles to 1,2-dienes, they found that the palladium-catalyzed hydrocarboxylation of aliphatic allenes provided substantial amounts of the 1,3-diene products instead of the anticipated allyl esters (Scheme 17a). For example, 1,1-disubstituted allene **66**, when treated with Pd_2dba_3 in the presence of a slight excess of acetic acid, resulted in a moderate yield of 1,3-diene **67** as a 1:1 mixture of *E*:*Z* isomers; similarly, the disubstituted aryl allenes **68**, under the same reaction conditions, resulted in 1,3-dienes **69** in 50% isolated yield.

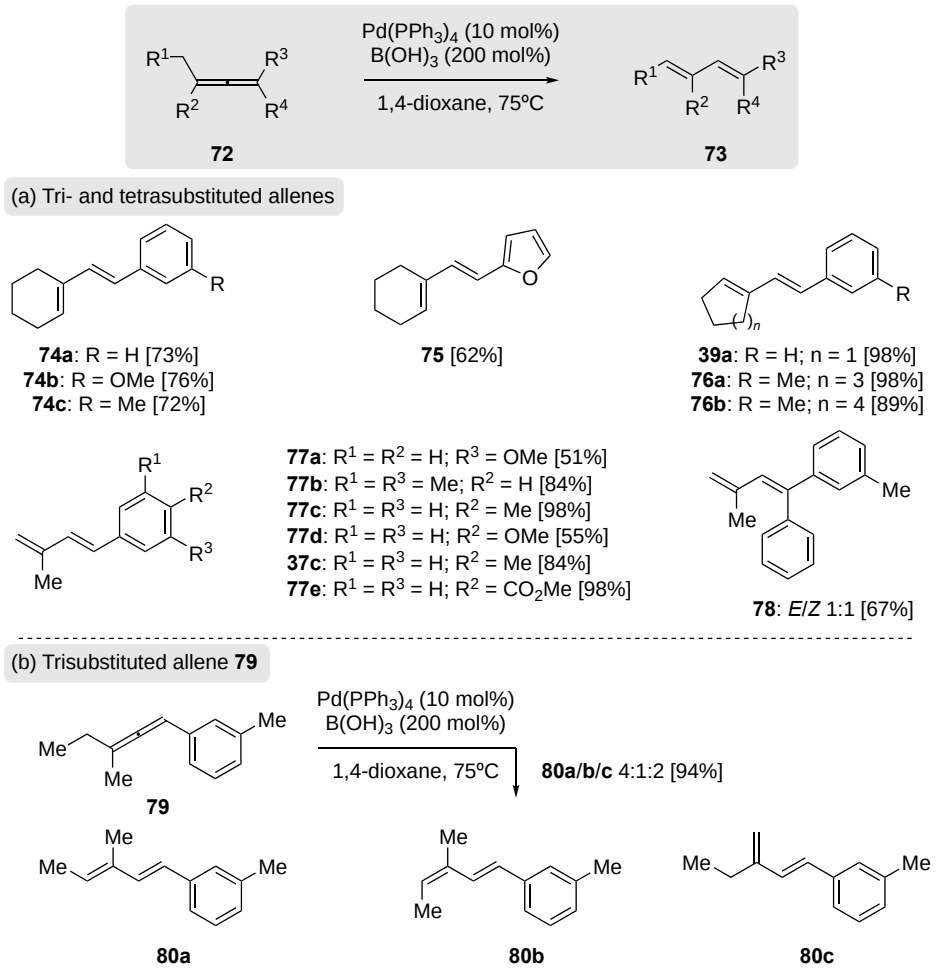


Scheme 17. (**a**) Yamamoto's observed rearrangement of allenes to 1,3-dienes through hydropalladation; (**b**,**c**) plausible mechanism for Yamamoto's rearrangement of allenes **66** and **68** via hydropalladation [67].

The authors postulated a plausible mechanism involving the initial formation of hydridopalladium species HPd(II)OAc, through the insertion of Pd(0) into HOAc; hydropalladiation of allenes **66** and **68** then provides π-allylpalladium intermediates **70** and **71**, respectively (Scheme 17b,c). In the case of π-allylpalladium intermediate **70**, β-hydride elimination of the allylic hydrogen can be accomplished to yield two possible intermediates, therefore producing 1,3-diene **67** as a 1:1 mixture of *E*:*Z* isomers; β-hydride elimination via the allylic hydrogen on adjacent methyl group was not observed. π-Allylpalladium intermediate **71** also undergoes β-hydride elimination of the allylic hydrogen, but this results in the formation of a single 1,3-diene **69**. This disclosure by Yamamoto of using an in situ formed H-Pd(II)OAc species to undertake a hydropalladiation-β-hydride elimination of an allene to generate 1,3-diene is significant. It demonstrated the potential of the Pd-catalyzed reaction pathway to achieve the rearrangement; however, it did suffer from the limited scope and, importantly, reaction selectivity over the more desired hydrocarboxylation pathway.

In 2018, Al-Jawaheri and Kimber disclosed a direct conversion of aryl allene **72** to 1,3-diene **73** using an H-Pd(II)-$OB(OH)_2$-mediated reaction manifold (Scheme 18) [68]. This transformation followed a previous report by the same authors on a base-free Pd coupling of arylboronic acid with propargylic alcohols, giving direct access to substituted 1,3-dienes (Scheme 19) [69]. After optimization, they found 200 mol% of boric acid in the presence of 10 mol% of Pd(0) could effectively rearrange a number of arylallenyl substrates to their 1,3-diene counterparts in good-to-excellent isolated yields, including tri- and tetra-substituted allenes (Scheme 18a). When tri-substituted allene **79** was exposed to the rearrangement

conditions, three 1,3-diene products were isolated, **80a**, **80b,** and **80c**, respectively, in a 4:1:2 ratio (Scheme 18b).



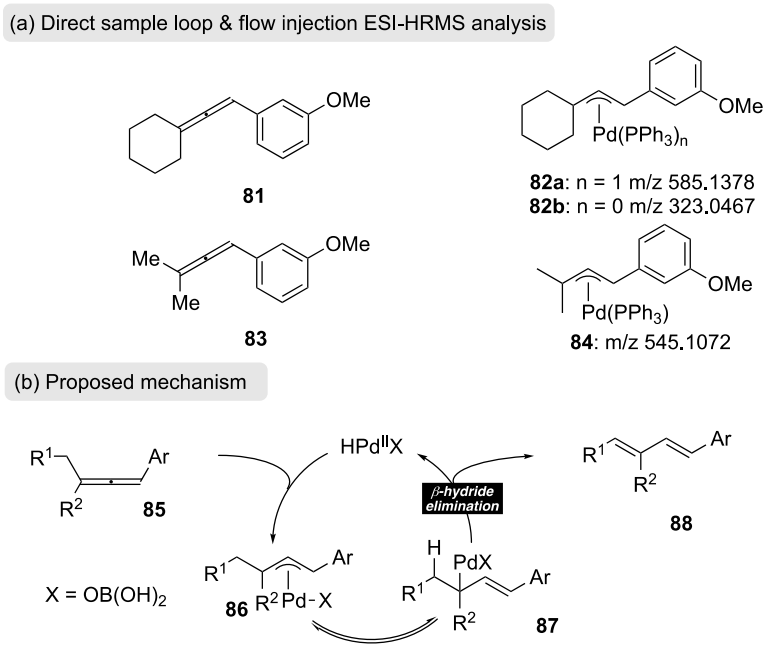
Scheme 18. (**a**) Substrate scope of the Pd(0)/boric acid mediated rearrangement; (**b**) product distribution for allene **79** [68].

The authors were also able to follow the course of the rearrangement using direct sample loop and flow injection ESI-HRMS analysis (Scheme 19a). Using this very sensitive technique, they analyzed the rearrangement of two arylallenes (**81** and **83**) whose selection was based on the presence of a meta-functional group (OMe) for adequate ionization. They were subsequently able to identify π-allylpalladium species **82** and **84** to further support the mechanism proposed in Scheme 19b. Accordingly, it was postulated that allene **85** undergoes hydropalladation with the Pd species H-$Pd^{II}OB(OH)_2$ to yield π-allylpalladium **86**, whose ultimate fate is to undergo a subsequent β-hydride elimination through intermediate **87**, resulting in the observed 1,3-diene **88**.

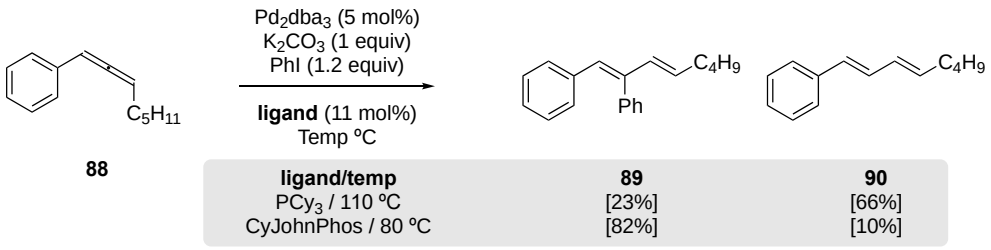
As with the Au-catalyzed method of Liu et al. [60,61], the scope of this rearrangement was limited to aryl-substituted allenes, illustrating the importance of the aryl substituent in stabilizing the intermediate π-allylpalladium species.

In a recent study by Vine and Schomaker [70], investigating Pd-catalyzed couplings between allenes and arylhalides, the authors observed significant amounts of 1,3-diene **90** instead of the desired Heck addition product **89** when exposing disubstituted allene **88** to the conditions shown in Scheme 20. During an optimization study, they observed the formation of **90** when undertaking the reaction with the electron-rich phosphine PCy_3; this could be suppressed when the ligand was exchanged for the more hindered phosphine CyJohnPhos, together with lowering of the reaction temperature and extending the reaction

time. The authors invoked the formation of a π-allylpalladium species in the formation of the undesired 1,3-diene **90**.



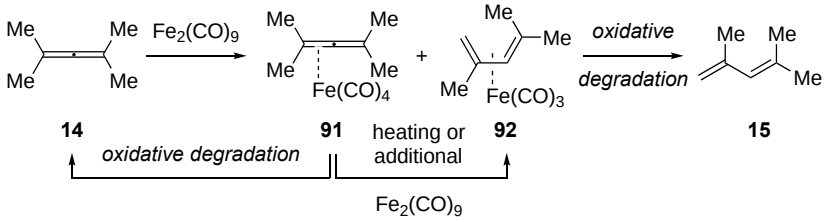
Scheme 19. (**a**) ESI-HRMS analysis using allenes **81** and **83**; (**b**) proposed mechanism.



Scheme 20. Observed rearrangement of allene **88** to 1,3-diene **90** under Heck-type coupling conditions [70].

4.3. Iron

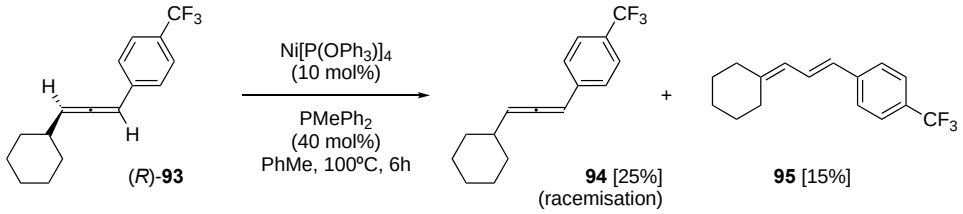
Pettit et al. observed that the reaction of tetramethylallene **14** with $Fe_2(CO)_9$ provided a mixture of two complexes, **91** and **92**, with **92** being the predominant product (Scheme 21) [71]. Furthermore, upon prolonged heating, or treatment with excess $Fe_2(CO)_9$, complex **91** could be converted to complex **92**. Oxidative degradation of each complex was then performed, with **91** providing the starting tetramethylallene (**14**), while complex **92** yielded 2,4-dimethyl-1,3-pentadiene **15**. This study established the effectiveness of $Fe_2(CO)_9$ to facilitate the allene to 1,3-diene rearrangement albeit with a stoichiometric amount of the metal complex.



Scheme 21. Pettit's observed rearrangement of tetramethylallene via oxidative degradation of iron complex **92** [71].

4.4. Nickel

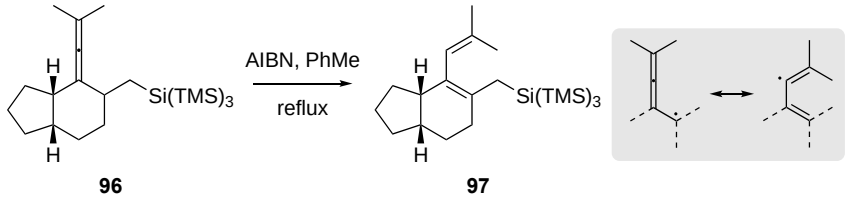
Nickel catalysis has been exploited to great effect to achieve the stereoselective hydrocyanation of allenes, with a π-allylnickel intermediate being key to this transformation [72]. This transformation can also be performed with enantiopure allenes with a good-to-excellent transfer of chiral information to the resultant products. When investigating the mechanistic basis of their Ni-catalyzed hydrocyanation of chiral allenes, Arai et al. performed their hydrocyanation reaction in the absence of a cyano source on enantiopure allene **93** (Scheme 22) [73]. As anticipated, the predominant product was racemic allene **94**, together with 15% of 1,3-diene **95**. The rationalization of the formation of **95** was through initial oxidative addition of Ni(0) to the allene followed by β-H elimination and reductive elimination to give the observed 1,3-diene **95**. In this study, the allene-to-1,3-diene rearrangement was only observed for a single substrate but does illustrate the potential for Ni(0) catalysis to achieve this transformation.



Scheme 22. The Ni(0)-facilitated rearrangement of enantio-enrich allene **93** [73].

5. Radical

Jones and Pattenden demonstrated that allene **96**, either as a mixture or as separate diastereoisomers, could undergo arrangement to 1,3-diene **97** using a catalytic amount of AIBN under reflux (Scheme 23) [74]. The authors postulate that allene **97** undergoes initial hydrogen abstraction to yield an allylic radical center that is propagated by an intermediate vinylic radical. This radical rearrangement manifold is reminiscent of the previously described thermal rearrangements of cyclopropylalkylidenes. Although this is an isolated example on one specific allenic substrate, it does illustrate the potential of a homolytic pathway to facilitate this allene-to-1,3-diene rearrangement.



Scheme 23. Pattenden's radical-mediated rearrangement of tetrasubstituted allene **96** [74].

6. Summary

This review discussed the rearrangement of alkylallenes to 1,3-dienes. The 1,3-diene motif continues to be an essential structural motif in organic chemistry, and therefore, innovative synthetic methods that can achieve its construction are essential. Contemporary synthetic methodologies continue to deliver structurally diverse allenes. Therefore, having the synthetic capability to rearrange them to their respective 1,3-dienes opens opportunities to access structurally diverse 1,3-dienes, hitherto inaccessible using traditional synthetic methods.

The early reports were acid or thermally mediated and are often substrate dependent, harnessing inherent ring strain or the participation of a remote heteroatom to achieve the rearrangement. Of the methods discussed to achieve this rearrangement, transition metals such as gold and palladium have displayed the greatest promise. They have good substrate scope for aryl-substituted allenes, where stabilization of the intermediate p-allyl is required. There are exceptions, such as the performance of 1,2-disubstituted

allenes in the gold-mediated pathway and the inability of haloboronic acid to participate cleanly in the palladium-mediated pathway. These two exceptions highlight the differing mechanistic pathways of each manifold. The gold(III)-mediated rearrangement of Lui et al. is predicated on the formation of a sufficiently stable carbocation, reflecting early acid-mediated reports of the rearrangement and subsequent DFT studies, whereas the palladium(0)-mediated methods are reliant on the formation of stable p-allylpalladium intermediates, with a subsequent β-hydride elimination of the allylic hydrogen to generate the thermodynamic 1,3-diene. The iron-mediated rearrangement of simple tetramethylallene requires further investigation regarding the scope and, importantly, needs to be rendered catalytic. In contrast, the nickel-mediated method can be achieved catalytically, but the scope of the reaction requires expansion. The AIBN-mediated rearrangement of a single tetraalkylallene shows promise given the recent development of mild photoredox methods for the generation of carbon-centered radicals.

More generally, the scope and generality of allenes that now can undergo rearrangement to their 1,3-dienes have been established. However, the successful application of this methodology requires further exploration, conceivably through target synthesis of natural products and functional materials. Additionally, it may be feasible to rearrange appropriately substituted allene substrates to provide new synthetic routes to much-sought-after polyene substrates, such as trienes and tetraenes.

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