

The Rearrangement of Alkylallenes to 1,3-Dienes

Subjects: Biochemical Research Methods

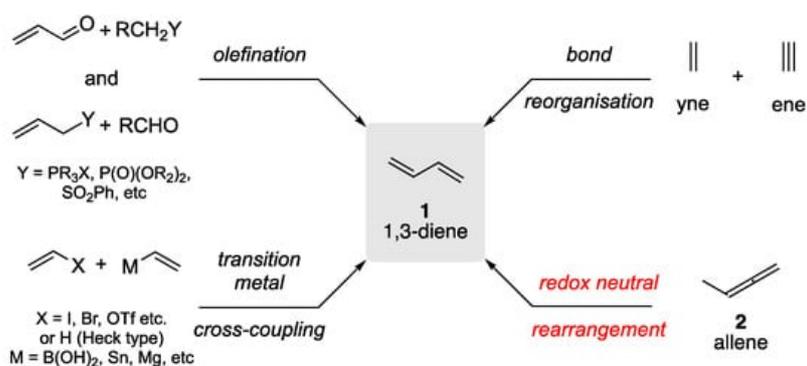
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1,3-Dienes are vital building blocks in organic synthesis. They underpin many fundamental synthetic transformations and are present in numerous natural products and drug candidate molecules.

Keywords: allene ; rearrangement ; stereoselective ; transition metal

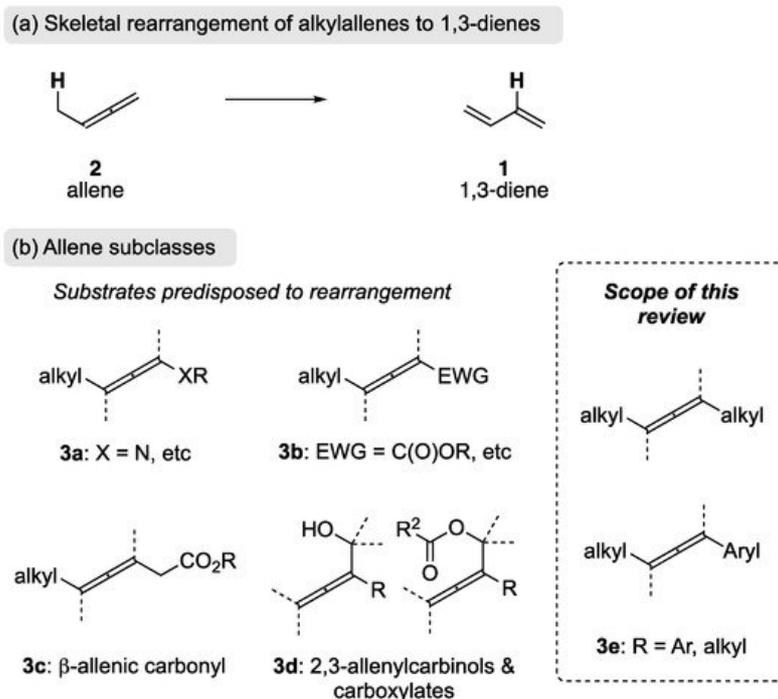
1. Introduction

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][2][3][4][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][7][8][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][12][13][14][15][16]; this was subsequently augmented by transition metal cross-coupling approaches [17][18][19][20][21], and the bond reorganization of appropriately substituted alkene and alkyne substrates [22][23][24][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.



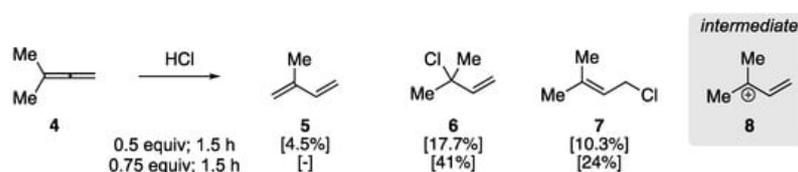
Scheme 2. (a) Rearrangement of an alkylallene to a 1,3-diene. (b) Different allene subclasses.

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][30][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 dienolic esters, which are present in several natural occurring pheromones and flavors [33][34][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][37][38], S_N2' pathways [39][40][41], and metal-mediated processes [42][43][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**).

2. Acid-Mediated Rearrangements

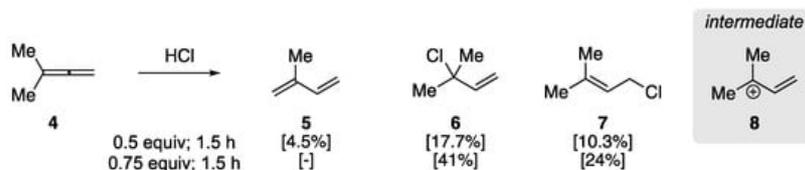
Acid-mediated rearrangements are primarily realized through the protonation of the central sp-hybridized carbon of the allene, where stabilization of a transient carbocation facilitates the formation of a thermodynamically stable 1,3-diene. This method, therefore, limits the scope of the allene substrates 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 (**5**) 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 $-78\text{ }^{\circ}\text{C}$ 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.



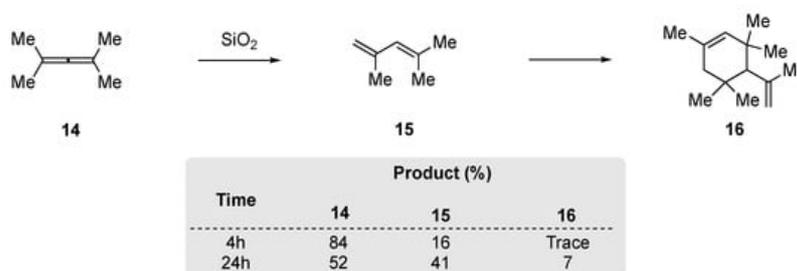
Scheme 3. Acid-catalyzed rearrangement of 3-methyl-1,2-butadiene **4** [47].

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.



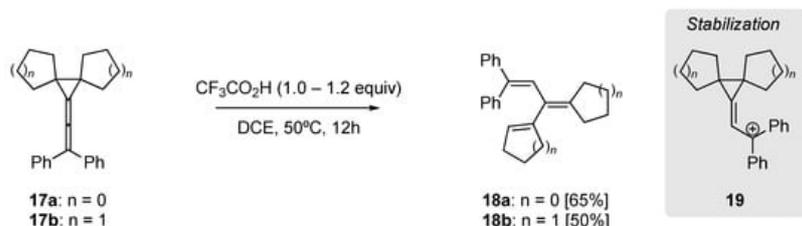
Scheme 4. HCl-promoted allene rearrangement. The rearrangement was facilitated by the presence of an electron-rich 4MeO-arene substituent^[48].

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**.



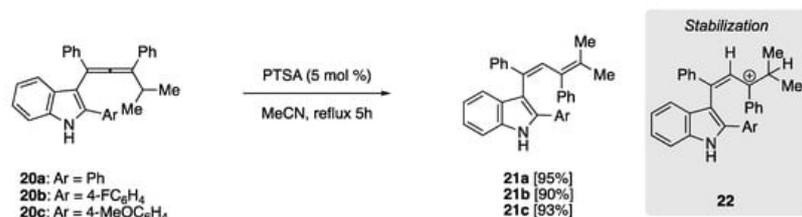
Scheme 5. SiO₂ rearrangement of tetramethylallene **14**^[49].

Li et al. utilized the intrinsic strain of diarylvinylicyclopropanes in their acid mediated rearrangement to yield trienes (Scheme 6)^[50]. For example, the dicyclopentyl (**17a**) and dicyclohexyl (**17b**) diarylvinylicyclopropanes 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.



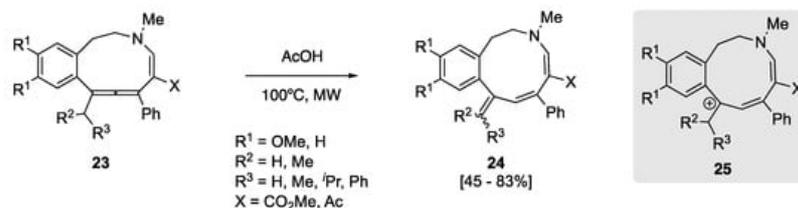
Scheme 6. Trifluoroacetic acid-mediated rearrangement of diaryl-vinylicyclopropanes^[50].

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 = 4-F-C₆H₄) or electron-rich (**20c**, Ar = 4-MeOC₆H₄) 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].

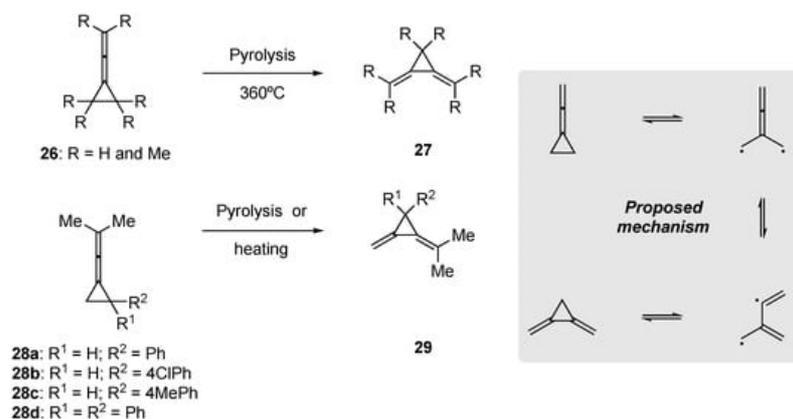
Titov et al., in a study examining the synthesis of potential bioactive tetrahydrobenzazecines, observed that cyclic allene **23** underwent rearrangement to 1,3-diene **24** upon microwave irradiation in acetic acid (Scheme 8) [52]. The yields were found to be good to excellent, depending on the substitution. 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

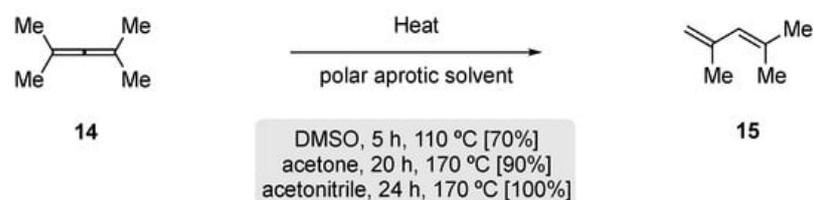
The rearrangement of strained allenic systems, such as the cyclopropyl allenes **26** and **28**, to 1,3-dienes has been known since the late 1960s (Scheme 9). Seminal works by Crandall and Paulson [53], Conia et al. [54], and Maitland Jones et al. [55] demonstrated that thermal rearrangements of strained *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][54][55].

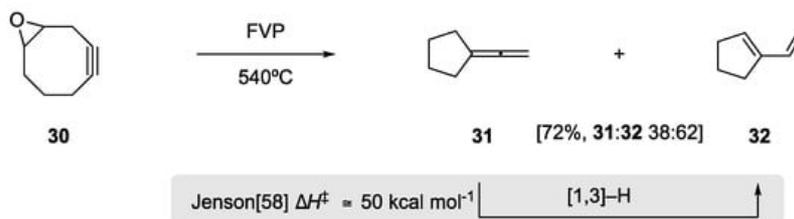
The synthetic utility of this transformation is limited. Rearrangement in these strained allenic systems (e.g., **28a–d**) benefits from aryl substitution on the cyclopropane, and this aligns well with the proposed mechanism to provide added stabilization in the radical process.

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-isopropylidencyclobutane. 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 allenenes in sigmatropic H shift, subsequently calculated an energy barrier of ΔH^\ddagger of $\cong 50$ 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].

References

- Deagostino, A.; Prandi, C.; Zavattaro, C.; Venturello, P. Functionalized 1-Alkoxy-1,3-dienes: Their Preparation and Applications in Synthetic Organic Chemistry. *Eur. J. Org. Chem.* 2006, 2006, 2463–2483.
- Nicolaou, K.C.; Snyder, S.A.; Montagnon, T.; Vassilikogiannakis, G. The Diels-Alder Reaction in Total Synthesis. *Angew. Chem. Int. Ed.* 2002, 41, 1668–1698.
- Negishi, E.; Huang, Z.; Wang, G.; Mohan, S.; Wang, C.; Hattori, H. Recent Advances in Efficient and Selective Synthesis of Di-, Tri-, and Tetrasubstituted Alkenes via Pd-Catalyzed Alkenylation-Carbonyl Olefination Synergy. *Acc. Chem. Res.* 2008, 41, 1474–1485.
- de Paolis, M.; Chataigner, I.; Maddaluno, J. Recent Advances in Stereoselective Synthesis of 1,3-dienes. In *Stereoselective Alkene Synthesis. Topics in Current Chemistry*; Wang, J., Ed.; Springer: Berlin/Heidelberg, Germany, 2012; Volume 327, pp. 87–146.
- Ghogare, A.A.; Greer, A. Using Singlet Oxygen to Synthesize Natural Products and Drugs. *Chem. Rev.* 2016, 116, 999–10034.
- Kobayashi, M.; Higuchi, K.; Murakami, N.; Tajima, H.; Aoki, S. Total synthesis of callistatin A, a potent cytotoxic polyketide from the marine sponge, *Callispongia truncata*. *Tetrahedron Lett.* 1997, 38, 2859–2862.
- Serhan, C.N. Pro-resolving lipid mediators are leads for resolution physiology. *Nature* 2014, 510, 92–101.
- Kupchan, S.M.; Komoda, Y.; Court, W.A.; Thomas, G.J.; Smith, R.M.; Karim, A.; Gilmore, C.J.; Haltiwanger, R.C.; Bryan, R.F. Maytansine, a Novel Antileukemic Ansa Macrolide from *Maytenus ovatus*. *J. Am. Chem. Soc.* 1972, 94, 1354–1356.
- Madden, K.S.; Mosa, F.A.; Whiting, A. Non-isoprenoid polyene natural products – structures and synthetic strategies. *Org. Biomol. Chem.* 2014, 12, 7877–7899.
- Soengas, R.G.; Rodriguez-Solla, H. Modern Synthetic Methods for the Stereoselective Construction of 1,3-Dienes. *Molecules* 2021, 26, 249–289.
- Maryanoff, B.E.; Reitz, A.B. The Wittig olefination reaction and modifications involving phosphoryl-stabilized carbanions. Stereochemistry, mechanism, and selected synthetic aspects. *Chem. Rev.* 1989, 89, 863–927.
- Ager, D.J. *Organic Reactions*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1990; pp. 1–223.
- Dong, D.-J.; Li, H.-H.; Tian, S.-K. A Highly Tunable Stereoselective Olefination of Semistabilized Triphenylphosphonium Ylides with N-Sulfonyl Imines. *J. Am. Chem. Soc.* 2010, 132, 5018–5020.
- Borg, T.; Tuzina, P.; Somfai, P. Lewis Acid-Promoted Addition of 1,3-Bis(silyl)propenes to Aldehydes: A Route to 1,3-Dienes. *J. Org. Chem.* 2011, 76, 8070–8075.
- Billard, F.; Robiette, R.; Pospíšil, J. Julia–Kocienski Reaction-Based 1,3-Diene Synthesis: Aldehyde-Dependent (E,E/Z)-Selectivity. *J. Org. Chem.* 2012, 77, 6358–6364.
- Zhou, R.; Wang, C.; Song, H.; He, Z. Wittig Olefination between Phosphine, Aldehyde, and Allylic Carbonates: A General Method for Stereoselective Synthesis of Trisubstituted 1,3-Dienes with Highly Variable Substituents. *Org. Lett.* 2010,

17. Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* 1995, 95, 2457–2483.
18. Lemhadri, M.; Battace, A.; Berthiol, F.; Zair, T.; Doucet, H.; Santelli, M. Palladium-Tetrphosphine Complex Catalysed Heck Reaction of Vinyl Bromides with Alkenes: A Powerful Access to Conjugated Dienes. *Synthesis* 2008, 7, 1142–1152.
19. Molander, G.A.; Felix, L.A. Stereoselective Suzuki–Miyaura Cross-Coupling Reactions of Potassium Alkenyltrifluoroborates with Alkenyl Bromides. *J. Org. Chem.* 2005, 70, 3950–3956.
20. Zheng, C.; Wang, D.; Stahl, S.S. Catalyst-Controlled Regioselectivity in the Synthesis of Branched Conjugated Dienes via Aerobic Oxidative Heck Reactions. *J. Am. Chem. Soc.* 2012, 134, 16496–16499.
21. Delcamp, J.H.; Gormisky, P.E.; White, M.C. Oxidative Heck Vinylation for the Synthesis of Complex Dienes and Polyenes. *J. Am. Chem. Soc.* 2013, 135, 8460–8463.
22. Diver, S.T.; Giessert, A.J. Enyne Metathesis (Enyne Bond Reorganization). *Chem. Rev.* 2004, 104, 1317–1382.
23. Zhang, L.; Sun, J.; Kozmin, S.A. Gold and Platinum Catalysis of Enyne Cycloisomerization. *Adv. Synth. Catal.* 2006, 348, 2271–2296.
24. Poulsen, C.S.; Madsen, R. Enyne Metathesis Catalyzed by Ruthenium Carbene Complexes. *Synthesis* 2003, 1, 1–18.
25. Trost, B.M.; Frederiksen, M.U.; Rudd, M.T. Ruthenium-Catalyzed Reactions—A Treasure Trove of Atom-Economic Transformations. *Angew. Chem. Int. Ed.* 2005, 44, 6630–6666.
26. Hayashi, R.; Hsung, R.P.; Feltenberger, J.B.; Lohse, A.G. Regio- and Stereoselective Isomerization of Allenamides: Synthesis of 2-Amido-Dienes and Their Tandem Isomerization-Electrocyclic Ring-Closure. *Org. Lett.* 2009, 11, 2125–2128.
27. Hayashi, R.; Feltenberger, J.B.; Lohse, A.G.; Walton, M.C.; Hsung, R.P. An efficient and practical entry to 2-amido-dienes and 3-amido-trienes from allenamides through stereoselective 1,3-hydrogen shifts. *Beilstein J. Org. Chem.* 2011, 7, 410–420.
28. Lu, T.; Lu, Z.; Ma, Z.-X.; Zhang, Y.; Hsung, R.P. Allenamides: A Powerful and Versatile Building Block in Organic Synthesis. *Chem. Rev.* 2013, 113, 4862–4904.
29. Trost, B.M.; Kazmaier, U. Internal redox catalyzed by triphenylphosphine. *J. Am. Chem. Soc.* 1992, 114, 7933–7935.
30. Hampton, C.S.; Harmata, M. Mechanistic Aspects of the Phosphine-Catalyzed Isomerization of Allenic Sulfones to 2-Arylsulfonyl 1,3-Dienes. *J. Org. Chem.* 2015, 80, 12151–12158.
31. Wang, Z.; Xu, X.; Kwon, O. Phosphine catalysis of allenes with electrophiles. *Chem. Soc. Rev.* 2014, 43, 2927–2940.
32. Hampton, C.S.; Harmata, M. Mechanistic Aspects of the Palladium-Catalyzed Isomerization of Allenic Sulfones to 1-Arylsulfonyl 1,3-Dienes. *J. Org. Chem.* 2016, 81, 4807–4822.
33. Tsuboi, S.; Masuda, T.; Takeda, A. Highly stereocontrolled synthesis of (2E,4Z)-dienoic esters with alumina catalyst. Its application to total syntheses of flavor components and insect pheromones. *J. Org. Chem.* 1982, 47, 4478–4482.
34. Amos, R.A.; Katzenellenbogen, J.A. Reaction of copper enolates of esters with propargylic systems. Facile preparation of 3,4-dienoic esters, stereoselective rearrangement to (2E,4Z)- and (2E,4E)-dienoic esters, and stereoselective synthesis of a fragrance from the Bartlett pear. *J. Org. Chem.* 1978, 43, 555–560.
35. Hendrick, C.A.; Willy, W.E.; McKean, D.R.; Baggiolini, E.; Siddall, J.B. Approaches to the synthesis of the insect juvenile hormone analog ethyl 3,7,11-trimethyl-2,4-dodecadienoate and its photochemistry. *J. Org. Chem.* 1975, 40, 8–15.
36. Alcaide, B.; Almendros, P.; Aragoncilli, C.; Redondo, M.C. Stereoselective Synthesis of 1,2,3-Trisubstituted 1,3-Dienes through Novel σ -Sigmatropic Rearrangements in α -Allenic Methanesulfonates: Application to the Preparation of Fused Tricyclic Systems by Tandem Rearrangement/Diels-Alder Reaction. *Eur. J. Org. Chem.* 2005, 1, 98–106.
37. Matsumoto, K.; Mizushima, N.; Yoshida, M.; Shindo, M. Stereocontrolled Synthesis of Multisubstituted 1,3-dienes via an Allene-Claisen Rearrangement. *Synlett* 2017, 28, 2340–2344.
38. Krafft, M.E.; Hallal, K.M.; Vidhani, D.V.; Cran, J.W. Gold(I)-catalysed Claisen rearrangement of allenyl vinyl ethers; synthesis of substituted 1,3-dienes. *Org. Biomol. Chem.* 2011, 9, 7535–7538.
39. Deng, Y.; Jin, X.; Fu, C.; Ma, S. Efficient Highly Selective Synthesis of Methyl 2-(Ethyne)alk-2-(E)-enoates and 2-(1'-Chlorovinyl)alk-2-(Z)-enoates from 2-(Methoxycarbonyl)2,3-allenols. *Org. Lett.* 2009, 11, 2169–2172.
40. Deng, Y.; Jin, X.; Ma, S. Studies on Highly Stereoselective Addition-Elimination Reactions of 3-(Methoxycarbonyl)-1,2-allen-4-ols with MX. An Efficient Synthesis of 3-(Methoxycarbonyl)-2-1,3(Z)-dienes. *J. Org. Chem.* 2007, 72, 5901–5904.

41. Horváth, A.; Backväll, J.E. Palladium(II)-Catalyzed SN2' Reactions of α -Allenic Acetates. Stereoconvergent Synthesis of (Z,E)-2-Bromo-1,3-dienes. *J. Org. Chem.* 2001, 66, 8120.
42. Zhang, X.; Fu, C.; Ma, S. Highly Stereoselective Facile Synthesis of 2-Acetoxy-1,3(E)-alkadienes via Rh(I)-Catalyzed Isomerization of 2,3-Allenyl Carboxylates. *Org. Lett.* 2011, 13, 1920–1923.
43. Buzas, A.K.; Istrate, F.M.; Gagosz, F. Gold(I)-Catalyzed Isomerization of Allenyl Carbinol Esters: An Efficient Access to Functionalized 1,3-Butadien-2-ol Esters. *Org. Lett.* 2007, 9, 985.
44. Wang, S.; Zhang, L. Gold-Catalyzed Efficient Formation of Alkenyl Enol Esters/Carbonates from Trimethylsilylmethyl-Substituted Propargyl Esters/Carbonates. *Org. Lett.* 2006, 8, 4585–4587.
45. Yu, S.; Ma, S. Allenes in Catalytic Asymmetric Synthesis and Natural Product Syntheses. *Angew. Chem. Int. Ed.* 2012, 51, 3074–3112.
46. Neff, R.K.; Frantz, D.E. Recent Advances in the Catalytic Syntheses of Allenes: A Critical Assessment. *ACS Catal.* 2014, 4, 519–528.
47. Jacobs, T.L.; Johnson, R.N. The Addition of Hydrogen Chloride to Aliphatic Allenic Hydrocarbons. *J. Am. Chem. Soc.* 1960, 82, 6397–6404.
48. Wenkert, E.; Leftin, M.H.; Michelotti, E.L. Synthesis of Allenes by Nickel-Catalyzed Grignard Reactions with Silylpropargyl Alcohols. *J. Org. Chem.* 1985, 50, 1122–1124.
49. Kropp, P.J.; Breton, G.W.; Craig, S.L.; Crawford, S.D.; Durland, W.F.; Jones, J.E.; Raleigh, J.S. Surface-Mediated Reactions. 6. Effects of Silica Gel and Alumina on Acid-Catalyzed Reactions. *J. Org. Chem.* 1995, 60, 4146–4152.
50. Li, W.; Shi, M.; Li, Y. Brønsted Acid Mediated Novel Rearrangements of Diarylvinyldenecyclopropanes and Mechanistic Investigations Based on DFT Calculations. *Chem. Eur. J.* 2009, 15, 8852–8860.
51. Sanz, R.; Miguel, D.; Martínez, A.; Gohain, M.; García-García, P.; Fernández-Rodríguez, M.A.; Álvarez, E.; Rodríguez, F. Brønsted Acid Catalyzed Alkylation of Indoles with Tertiary Propargylic Alcohols: Scope and Limitations. *Eur. J. Org. Chem.* 2010, 36, 7027–7039.
52. Titov, A.A.; Kobzev, M.S.; Borisova, T.N.; Listratova, A.V.; Evenko, T.V.; Varlamov, A.V.; Voskressensky, L.G. Facile Methods for the Synthesis of 8-Ylidene-1,2,3,8-tetrahydrobenzazecines. *Eur. J. Org. Chem.* 2020, 20, 3041–3049.
53. Crandall, J.K.; Paulson, D.R. The Pyrolysis of Alkenyldenecyclopropanes. A Convenient Synthesis of Dimethylenecyclopropanes. *J. Am. Chem. Soc.* 1966, 88, 4302–4303.
54. Bloch, R.; le Perchec, P.; Conia, J.-M. Dimethylenecyclopropane. *Angew. Chem. Int. Ed. Engl.* 1970, 9, 798–799.
55. Jones, M.; Hendrick, M.E.; Hardie, J.A. Pyrolysis of Phenylalkenyldenecyclopropanes. *J. Org. Chem.* 1971, 36, 3061–3062.
56. Taylor, D.R.; Wright, D.B. Thermal Cycloadditions and Isomerisation of Tetramethylallene. *Chem. Commun.* 1968, 8, 434–435.
57. Meier, H.; Schmitt, M. Cycloalkin-vinyldenecycloalkan-Umlagerungen. *Tetrahedron Lett.* 1989, 30, 5873–5876.
58. Jensen, F. A Theoretical Study of the Allene Effect in Sigmatropic Hydrogen Shifts. *J. Am. Chem. Soc.* 1995, 117, 7487–7492.

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