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Synthetic Methods

Allenols versus Allenones: Rhodium-Catalyzed Regiodivergent and Tunable Allene Reactivity with Triazoles

Benito Alcaide,*[a] Pedro Almendros,*[b] Sara Cembellín,[a] Teresa Martínez del Campo,[a] and Guillermo Palop[a]

Dedication ((optional))

Abstract: 2-Pyrrolines and 6-oxo-hexa-2,4-dienals have been prepared through the divergent reactions of 1-benzenesulfonyl-4-aryl-1,2,3-triazoles with functionalized allenes. The rhodium-catalyzed reactions between allenols and 1-benzenesulfonyl-4-aryl-1,2,3-triazoles yielded 2-pyrrolines. This transformation is compatible with the presence of aliphatic, aromatic, heterocyclic, amide, and halogen functional groups. Interestingly, a reactivity switch took place when the allene-tethered alcohol substrate was replaced by its ketone counterpart. When the rhodium-catalyzed reaction of 1-benzenesulfonyl-4-phenyl-1,2,3-triazole was performed with allenones, acyclic 6-oxo-hexa-2,4-dienals were stereoselectively formed as (2*Z*,4*E*) isomers.

Introduction

N-Sulfonyl-1,2,3-triazoles are important synthetic intermediates, which have been used as latent α-imino metal carbenes for the preparation of a vast array of functionalized organic compounds.[1] On the other hand, despite regioselectivity issues, the allene moiety has attracted much attention due to its chamaleonic reactivity, which results in a variety of synthetically useful transformations.[2] Numerous examples on the metal-catalyzed transannulation reactions of *N*-sulfonyl-1,2,3-triazoles with different functional groups have been described. However, to the best of our knowledge there is just three reports on the reactivity of this heterocycle with the allene scaffold (Scheme 1a).[3] Taking into account that the intermolecular transannulation reaction reported by Miura and Murakami is limited to simple monosubstituted allenes,[3b] we decide to test the reactivity of more functionalized allenes, namely, α-allenols and α-allenones (Scheme 1b). Although catalytic triazole transannulation with 1,2-dienes bearin an additional nucleophilic center is attractive, it may b troublesome due to additional selectivity problems. Herein, w describe the rhodium-catalyzed reactions of 1-benzenesulfonyl-4 aryl-1,2,3-triazoles with allene-tethered alcohols or ketones, whic provide a divergent synthetic protocol for the construction of 2 pyrrolines or 6-oxo-hexa-2,4-dienals through controllable α-imin metal carbene related processes.

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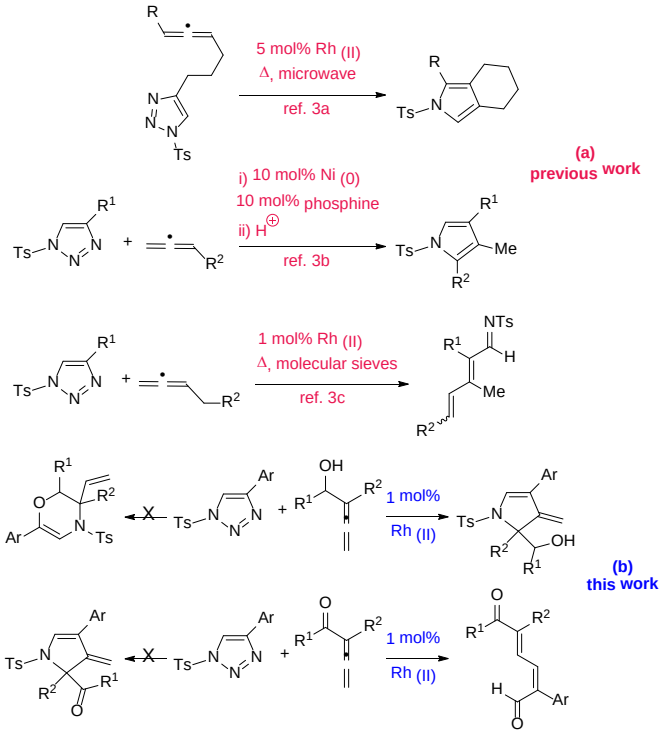

Scheme 1. Transannulation reactions of *N*-sulfonyl-1,2,3-triazoles with allenes.

Results and Discussion

Starting allenols **1a–i** were easily prepared from the appropriate aldehyde and a conveniently substituted 1-bromo-2-propyne through indium-promoted reaction under Barbier conditions.[4] Allenones **2** were readily obtained by oxidation of allenols **1** with Dess–Martin periodinane.[5] Initially, we surveyed whether allenol **1a** was a competent substrate to be engaged in the metal-catalyzed reaction with *N*-sulfonyl-1,2,3-triazole **3a**. This assumption exhibits some troubles and displays an obstacle because of the competitive and well-known O–C cyclization of allenols in the presence of metals.[6] Happily, the $Rh_2(oct)_4$-catalyzed reaction proceeded smoothly in toluene at reflux temperature to afford the 2-pyrroline derivative **4aa** (Scheme 2) as a separable mixture (80:20) of diastereomers. The aromatization was blocked by the methyl group at the newly generated quaternary streocenter. Different solvents such as $CHCl_3$ or 1,4-dioxane were not as effective as toluene. Poor performance was achieved with the use of different promoters such as $Cu(OTf)_2$ or $AgNTf_2$. When the loading of rhodium salt was augmented from 1 mol% to 5 mol%, it resulted in a negligible yield increasement. Our next ain was to investigate the generality of the 2-pyrroline formation reaction by variation of the allenol substitution pattern. In the event, a variety of allenols were probed to give the non-aromatic heterocyclic products **4aa–ai** in reasonable yields (Scheme 2). The stereoselectivities of the reactions of allenols **1a–i** derived from aromatic aldehydes with triazoles **3a,b** were found to be modest, and the best result was obtained (selectivity *ca.* 85:15) from the reactions between allenol-tethered indoles **1h** and **1i** with *N*-sulfonyl-1,2,3-triazole **3a** (Scheme 2). The rhodium-catalyzed reaction of tertiary allenol **1j** with *N*-sulfonyl-1,2,3-triazole **3a** was troublesome, and give a complicated mixtures of unidentified products (Scheme 3). Probably, the highly encumbered indolone-tethered allenol **1j** did not afford the 2-pyrroline **4ja** because of steric reasons, due to the presence of the tertiary stereocenter proximal to the reactive side. Interestingly, the reactions of allenols **1k–m** derived from aliphatic aldehydes with triazole **3a** afforded the required 2-pyrrolines **4ka–ma** with a very high selectivity -by our detection method through NMR the other diastereomer could not be detected-, but in moderate yields (Scheme 3). The rhodium-catalyzed reaction between 1-phenyl-1-methyl-1,2-propadiene, a 1,1-disubstituted allene which lacks th hydoxy group, and triazole **3a** was not very competent and led to complicated mixture (Scheme 3). In order to know the influence c the hydroxyl group, the allenyl ether **1b-Me** derived from protectio of the OH in allenol **1b** was employed (Scheme 3). The absence c the free alcohol has a negative impact in the reactivity because n pyrroline **4ba-Me** was detected when allene **1b-Me** was treate with *N*-sulfonyl-1,2,3-triazole **3a** in presence of $Rh_2(oct)_4$. Startin allene **1b-Me** remained unreactive after 2 hours (the required tim for completion of the reaction of allenol **1b**), and under prolonge heating the only products observed were derived fror decomposition of triazole **3a**. Tentatively, the failure of the OMe allene **1b-Me** should be attributed to the absence of a beneficia coordinative interaction between the rhodium and the OH grou which is present in allenols such as **1b**, presumably in the transier species formed after the attack of the allene moiety to th rhodacarbene. Unfavorable steric reasons may also be operative

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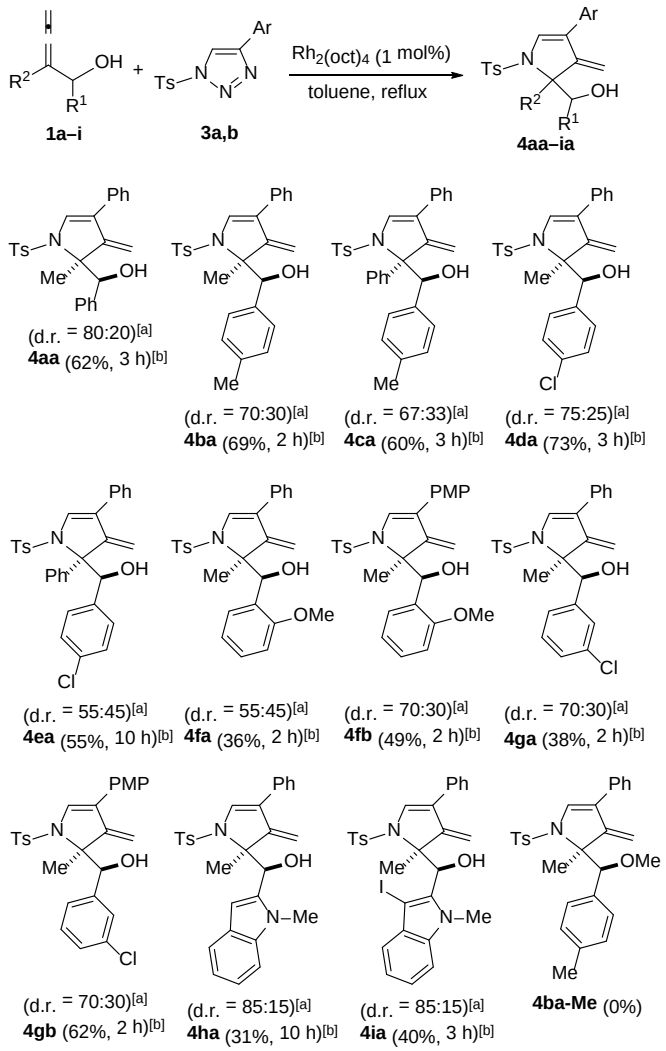
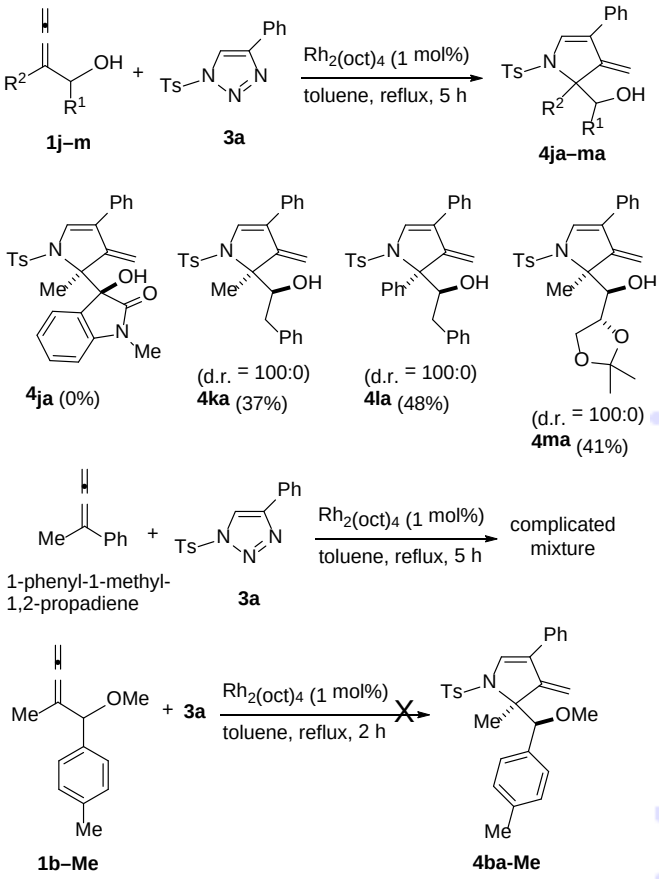


Scheme 2. Rhodium-catalyzed reaction of allenols **1a–i** (R^1 = Ar) with triazoles **3**. Controlled synthesis of 2-pyrrolines **4aa–ia**. PMP = $4MeOC_6H_4$. [a] The mixture of diastereomers was separated by column chromatography. [b] Major diastereomer shown. Yields refers to major isomer, isolated as pure product with correct analytical and spectroscopic data. Minor isomer could not be isolated as pure material.



Scheme 3. Rhodium-catalyzed reaction of allenols **1j–m** (R^1 = alkyl) with triazol **3a**. Controlled synthesis of 2-pyrrolines **4ja–ma**.

Having found a reliable method for the synthesis of 2 pyrrolines **4** through the coupling of allenols **1** with *N*-sulfonyl-1,2,3 triazoles **3**, we decide to undertake the study of a different type c allenes, namely, allenones **2**. However, allenones can react unde rhodium-, silver-, gold-, and palladium-catalyzed conditions to forr new O–C bonds through traditional cycloisomerization paths resulting in furans.[5],[7] Given this established reactivity, we face potential problem in the form of a rival cyclization reaction. Takin into account the high affinity of rhodium salts toward *N*-sulfony 1,2,3-triazoles, we envisioned that the reaction of th azaheterocycle **3** with the metallic catalyst should take place firs thus making feasible our synthetic design. Under the optimize reaction conditions for allenols **1**, complete consumption of th starting allenone **2a** in presence of *N*-sulfonyl-1,2,3-triazole **3a** wa observed. Noteworthy, lack of formation of the cyclic product o type **4** was observed under $Rh_2(oct)_4$ catalysis. In the event, the 1,6-dicarbonyl derivative **5a** was formed instead as single isomer but in a low 25% yield. Consequently, a notable effect on the outcome of the reaction was evidenced due to the different electronic character of the allene precursor. This initial experiment settled the viability of a substrate-controlled divergent allene reactivity, but the low yield of the final product is a serious limitation for its synthetic utility. Fortunately, the efficiency of the reaction was improved with the modification of the solvent (chloroform rather than toluene). Scheme 4 outlines the preparation of several 6-oxo-hexa-2,4-dienals **5**. The imine functionality in **5m-imin** survived the

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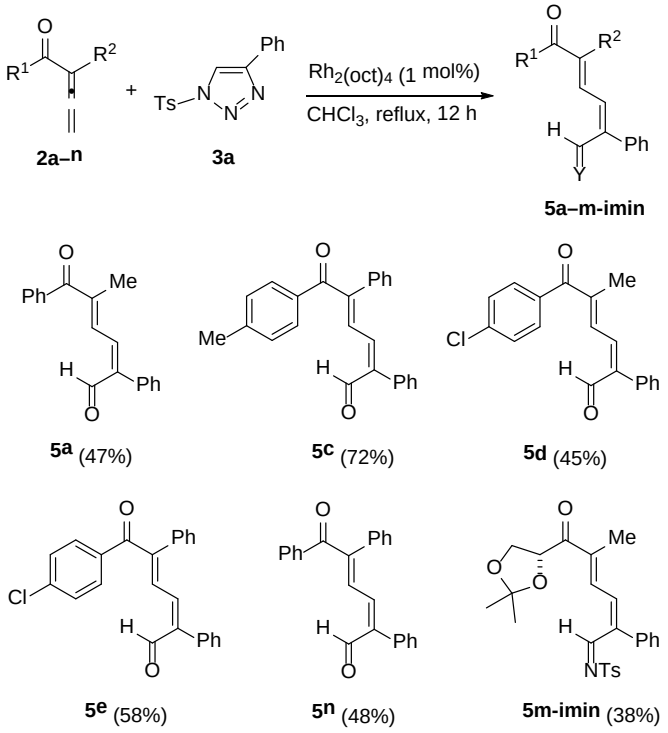
reaction conditions and the chromatographic purification, but the final iminoketone adduct was isaolated in diminished yield. Cycloisomerization adducts, namely, furans were detected in all cases as minor side products (*ca.* 5%) by TLC and ^{1}HNMR analyses of the crude reaction mixtures. Unlike allenols **1**, which undergo triazole transannulation reactions, allenones **2** displayed a different type of reactivity, enabling the synthesis of 1,6-dicarbonyls **5**.[8] Adducts **5** were obtained in a totally stereoselective fashion as single (2*Z*,4*E*) isomers. The structure and stereochemistry of 6-oxo-hexa-2,4-dienal **5d** was unambiguously assigned through its X-ray crystallographic analysis (Figure 1).[9]



Scheme 4. Rhodium-catalyzed reaction of allenones **2** with triazole **3a**. Controlled synthesis of 1,6-dicarbonyl derivatives **5**.

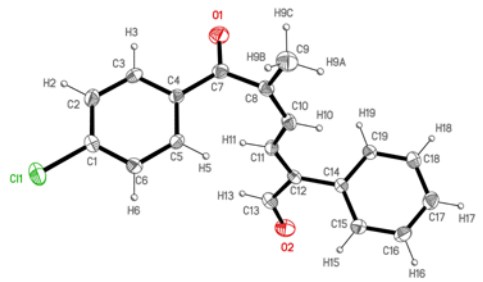
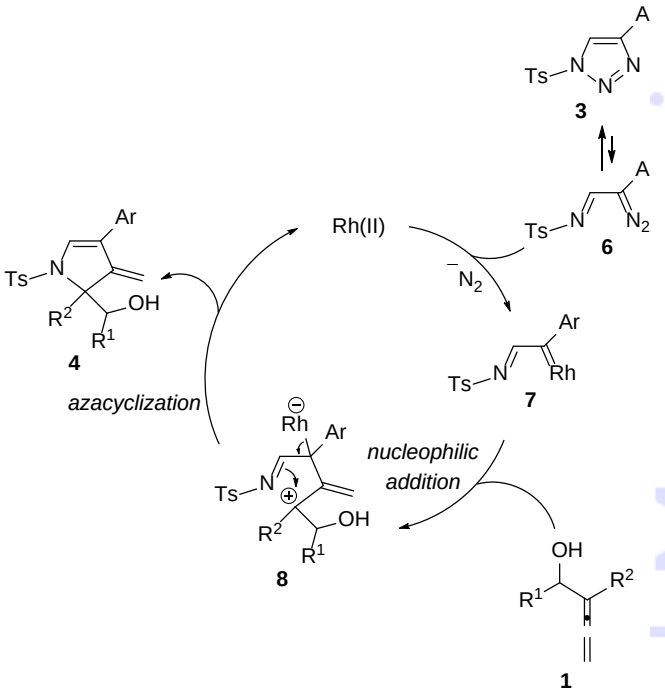


Figure 1. ORTEP drawing of (2*Z*,4*E*)-6-(4-chlorophenyl)-5-methyl-6-oxo-2-phenylhexa-2,4-dienal **5d**. Thermal ellipsoids shown at 50% probability.

A plausible mechanistic proposal for the rhodium-catalyzed formation of 2-pyrrolines **4** from allenols **1** and *N*-sulfonyl-1,2,3-triazoles **3** is depicted in Scheme 5. Initially, reaction of the $Rh_2(oct)_4$ catalyst with the appropriate *N*-sulfonyl-1,2,3-triazole **3**, which is in equilibrium with its α-imino tautomer **6**, results in the formation of an α-imino Rh(II)-carbene **7** after extrusion of dinitrogen. Nucleophilic addition of the internal double bond of the cumullene moiety in allenols **1** to rhodacarbenes **7** formed zwitterions **8**. Species **8** suffer a regioselective azacyclization reaction through attack of the imine moiety towards the positively charged allylic carbon atom to give 2-pyrrolines **4** with concurrent regeneration of the rhodium(II) catalyst.[10]



Scheme 5. Mechanistic explanation for the formation of 2-pyrrolines **4**.

A tentative mechanistic proposal for the generation of 6-oxo hexa-2,4-dienals **5** from allenones **2** and *N*-sulfonyl-1,2,3-triazol **3a** under $Rh_2(oct)_4$ catalysis is summarized in Scheme 6. Th required formation of the α-imino Rh(II)-carbene **7** occurs in th same way that above. However, replacing the allenol by a allenone resulted in a switch of the reactivity. A positiona selectivity reversal should occur by attack of the terminal doubl bond of the allenone **2** to the electrophilic center of th rhodacarbene **7**. In this way, it may be formed zwitterionic specie **9**, which suffer a 1,2-hydride shift to its isomeric zwitterion **10** which rapidly evolves to the 1,6-dicarbonyl derivative **5** afte release of the metal catalyst. The unforeseen isolation of imine **5m-imin** from allenone **2m** may reforce the pathway depicted in Scheme 6. An alternative mechanistic possibility to the attack of the electrophilic carbon of compound **7** to the end of the allene, which should be contemplated, is an initial cyclopropanation of the terminal double bond of the allene.[11]

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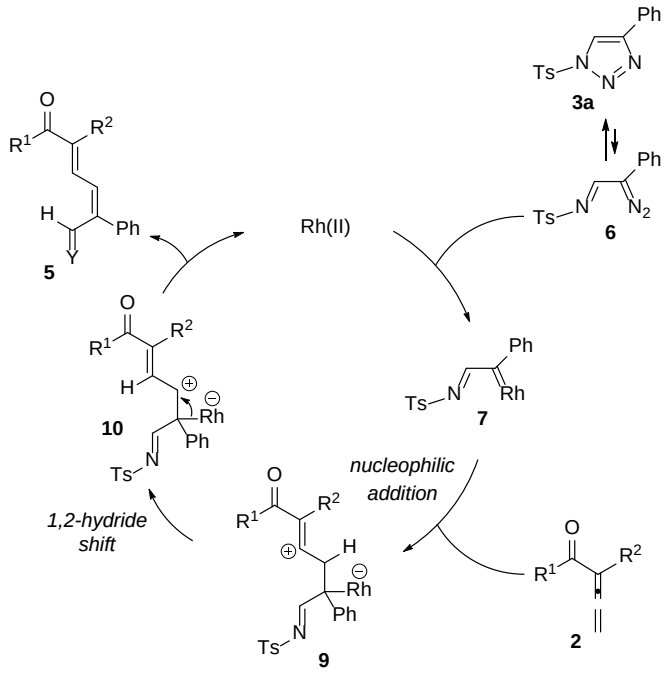

Scheme 6. Mechanistic explanation for the formation of 6-oxo-hexa-2,4-dienals **5**.

Conclusion

In conclusion, we report that the divergent reaction of 1-benzenesulfonyl-4-aryl-1,2,3-triazoles with functionalized allenes has selectively afforded 2-pyrrolines and 6-oxo-hexa-2,4-dienals. The rhodium-catalyzed reactions between allenols and 1-benzenesulfonyl-4-aryl-1,2,3-triazoles yielded 2-pyrrolines, while a reactivity switch took place when the allene-tethered alcohol substrate was replaced by its ketone counterpart. Thus, acyclic 6-oxo-hexa-2,4-dienals were stereoselectively formed as (2*Z*,4*E*) isomers when the rhodium-catalyzed reaction of 1-benzenesulfonyl-4-phenyl-1,2,3-triazole was performed with allenones. Items for future study of this reactivity switch comprise the analysis of additional factors which influence the reaction outcome, election of different allene substrates, and mechanistic details.

Experimental Section

General methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or Varian VRX-300S. NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{1}H, 7.27 ppm; ^{13}C, 76.9 ppm), or C_6D_6 (^{1}H, 7.16 ppm; ^{13}C, 128.0 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. X-Ray crystallographic data were collected on a Bruker Smart CCD difractomer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 Kv and 35 mA with an exposure of 30.18 s in ω. Specific rotation $[\alpha]_D$ is given in 10^{-1} deg cm^2 g^{-1} at 20 °C, and the concentration (*c*) is expressed in g per 100 mL. All commercially available compounds were used without further purification.

General procedure for the synthesis of 2-pyrrolines 4. $Rh_2(Oct)_4$ (0.001 mmol) and the appropriate triazole **3** (0.10 mmol) were added to a stirred solution of the corresponding allenol **1** (0.11 mmol) in toluene (1.0 mL) under argon. The resulting mixture was stirred under argon atmosphere at reflux temperature until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 x 3 mL), and the combined extracts were washed twice with brine. The organic layer was dried ($MgSO_4$) an concentrated under reduced pressure. Chromatography of the residue elutin with hexanes/ethyl acetate mixtures gave analytically pure compounds Spectroscopic and analytical data for 2-pyrrolines **4** follow.[12]

2-Pyrroline 4ba. From 51 mg (0.30 mmol) of allenol **1b**, and after flas chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gav compound **4ba** (92 mg, 69%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 °C δ = 7.77 (m, 4H, Ar), 7.33 (s, 1H, =CH), 7.22 (d, 1H, *J* = 8.1 Hz, Ar), 7.00 (d, 2H *J* = 8.2 Hz, Ar), 6.90 (m, 3H, Ar), 6.61 (d, 2H, *J* = 8.0 Hz, Ar), 6.13 (br s, 1H, OCH 5.02 (s, 1H, =C*H*H), 4.93 (s, 1H, =CH*H*), 2.12 (s, 3H, Me), 1.81 (s, 3H, Me), 1.7 (s, 3H, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 195.5, 146.1, 142.9, 138.5 136.8, 135.2, 135.1, 134.0, 133.4 (=CH), 129.9 (Ar, 2CH), 129.5 (Ar, 2CH), 129. (Ar, 2CH), 128.7 (Ar, 2CH), 128.6 (Ar, CH), 128.3 (Ar, 2CH), 127.8 (Ar, 2CH 117.7 (=CH_2), 59.9 (OCH), 21.2 (Me), 21.0 (Me), 16.2 (Me); IR ($CHCl_3$): ν = 327 1684, 1594 cm^{-1}; HRMS (ES): calcd for $C_{27}H_{27}NO_3S$ [*M* + H]$^+$: 446.1790; found 446.1773.

2-Pyrroline 4ca. From 67 mg (0.28 mmol) of allenol **1c**, and after flas chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gav compound **4ca** (85 mg, 60%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 °C δ = 7.56 (d, 2H, *J* = 8.3 Hz, Ar), 7.41 (d, 2H, *J* = 8.0 Hz, Ar), 7.35 (dd, 1H, *J* = 8.3 1.2 Hz, Ar), 7.23 (m, 1H, Ar), 7.10 (m, 2H, Ar), 7.02 (d, 3H, *J* = 8.0 Hz, Ar), 6.9 (m, 3H, Ar), 6.75 (t, 2H, *J* = 7.9 Hz, Ar), 6.53 (s, 1H, =CH), 6.47 (d, 2H, *J* = 8. Hz, Ar), 5.80 (s, 1H, OCH), 5.61 (s, 1H, =C*H*H), 5.25 (s, 1H, =CH*H*), 2.11 (s, 3H Me), 1.65 (s, 3H, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 197.5, 142.9, 142.4 141.4, 139.4, 138.0, 137.6, 135.8, 134.2, 133.4 (=CH), 131.3 (Ar, CH), 129.6 (A 2CH), 129.5 (Ar, 2CH), 129.1 (Ar, 2CH), 128.9 (Ar, 2CH), 128.6 (Ar, 2CH), 128. (Ar, 2CH), 128.2 (Ar, CH), 127.9 (Ar, 2CH), 127.7 (Ar, 2CH), 121.3 (=CH_2), 59. (OCH), 21.2 (Me), 20.9 (Me); IR ($CHCl_3$): ν = 3280, 1685, 1595 cm^{-1}; HRM (ES): calcd for $C_{32}H_{29}NO_3S$ [*M* + H]$^+$: 508.1946; found: 508.1940.

2-Pyrroline 4la. From 95 mg (0.40 mmol) of allenol **1l**, and after flas chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gav compound **4la** (99 mg, 48%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 °C δ = 7.68 (t, 4H, *J* = 8.2 Hz, Ar), 7.05 (m, 10H, Ar), 6.91 (m, 3H, Ar), 6.60 (d, 2H *J* = 7.9 Hz, Ar), 6.06 (d, 1H, *J* = 8.5 Hz, =CH), 5.96 (d, 1H, *J* = 8.5 Hz, OCH), 4.9 (s, 1H, =C*H*H), 4.75 (s, 1H, =CH*H*), 3.22 (m, 2H, =CH_2), 1.78 (s, 3H, Me); ^{13} NMR (75 MHz, C_6D_6, 25 °C): δ = 195.2, 145.6, 142.8, 140.7, 140.5, 138.6, 138.5 135.0, 133.5 (=CH), 130.0 (Ar, 2CH), 129.9 (Ar, 2CH), 129.6 (Ar, 2CH), 129.5 (Ar, 2CH), 128.8 (Ar, 2CH), 128.7 (Ar, 2CH), 128.6 (Ar, 2CH), 128.5 (Ar, 2CH), 127.6 (Ar, 2CH), 126.4 (Ar, CH), 120.9 (=CH_2), 60.0 (OCH), 36.1 (CH_2), 21.0 (Me); IR ($CHCl_3$): ν = 3279, 1686, 1595 cm^{-1}; HRMS (ES): calcd for $C_{32}H_{30}NO_3S$ [*M* + H]$^+$: 508.1941; found: 508.1949.

2-Pyrroline 4ma. From 100 mg (0.54 mmol) of allenol **1m**, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **4ma** (100 mg, 41%) as a colorless oil; $[\alpha]_D^{20}$ = +16.7 (*c* 0.3 in $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.76 (d, 2H, *J* = 8.3 Hz, Ar), 7.72 (d, 2H, *J* = 7.1 Hz, Ar), 6.93 (m, 3H, Ar), 6.68 (d, 2H, *J* = 8.5 Hz, Ar), 6.16 (d, 1H, *J* = 8.8

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Hz, OH), 6.02 (d, 1H, *J* = 7.3 Hz, =CH), 5.91 (d, 1H, *J* = 8.6 Hz, OCH), 4.92 (s, 1H, =C*H*H), 4.90 (s, 1H, =CH*H*), 4.67 (q, 1H, *J* = 7.5 Hz, OCH), 3.88 (t, 1H, *J* = 7.7 Hz, CH*H*), 3.50 (t, 1H, *J* = 7.7 Hz, C*H*H), 1.80 (s, 3H, Me), 1.52 (s, 3H, Me), 1.47 (s, 3H, Me), 1.38 (s, 3H, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 ºC): δ = 195.4, 145.7, 142.9, 138.6, 137.0, 135.0, 133.5 (=CH), 129.3 (Ar, 2CH), 128.5 (Ar, 2CH), 128.4 (Ar, 2CH), 128.0 (Ar, CH), 127.5 (Ar, 2CH), 118.1 (=CH_2), 109.4, 73.4 (OCH), 69.6 (OCH_2), 60.2 (OCH), 27.0 (Me), 26.3 (Me), 21.0 (Me), 15.4 (Me); IR ($CHCl_3$): ν = 3281, 1685, 1593 cm^{-1}; HRMS (ES): calcd for $C_{25}H_{33}N_2O_5S$ [*M* + NH_4]$^+$: 473.2105; found: 473.2114.

General procedure for the synthesis of 6-oxo-hexa-2,4-dienals 5. $Rh_2(Oct)_4$ (0.001 mmol) and the appropriate triazole **3** (0.10 mmol) were added to a stirred solution of the corresponding allenone **2** (0.11 mmol) in choroform (1.0 mL) under argon. The resulting mixture was stirred under argon atmosphere at reflux temperature until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 x 3 mL), and the combined extracts were washed twice with brine. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data 6-oxo-hexa-2,4-dienals **5** follow.

6-Oxo-hexa-2,4-dienal 5a. From 40 mg (0.25 mmol) of allenone **1a**, and after flash chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **5a** (33 mg, 47%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ = 8.93 (s, 1H, CHO), 7.84 (d, 2H, *J* = 8.4 Hz, Ar), 7.19 (m, 3H, Ar), 7.08 (m, 5H, Ar), 6.74 (d, 1H, *J* = 12.0 Hz, =CH), 6.45 (dd, 1H, *J* = 12.0, 1.5 Hz, =CH), 1.60 (d, 3H, *J* = 1.3 Hz, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 ºC): δ = 197.9 (CO), 192.0 (CHO), 148.0, 143.0 (=CH), 142.7, 136.3, 133.9 (Ar, CH), 132.8, 130.5 (Ar, 2CH), 129.6 (Ar, 2CH), 129.2 (Ar, 2CH), 128.5 (Ar, 2CH), 128.4 (Ar, CH), 126.4 (=CH), 21.8 (Me); IR ($CHCl_3$): ν = 1704, 1689, 1655, 1619 cm^{-1}; HRMS (ES): calcd for $C_{19}H_{16}O_2$ [*M* + H]$^+$: 277.1223; found: 277.1221.

6-Oxo-hexa-2,4-dienal 5c. From 33 mg (0.14 mmol) of allenone **1c**, and after flash chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **5c** (37 mg, 72%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ = 9.02 (s, 1H, CHO), 7.98 (d, 2H, *J* = 8.2 Hz, Ar), 7.22 (m, 4H, Ar), 7.21 (d, 1H, *J* = 12.0 Hz, =CH), 7.12 (m, 4H, Ar), 7.05 (d, 1H, *J* = 12.0 Hz, =CH), 6.86 (m, 2H, Ar), 6.84 (t, 2H, *J* = 7.9 Hz, Ar), 1.91 (s, 3H, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 ºC): δ = 196.4 (CO), 191.9 (CHO), 150.1, 145.2, 144.0, 143.0 (=CH), 136.5, 134.8, 132.7, 130.7 (Ar, 2CH), 130.2 (Ar, 2CH), 130.0 (Ar, 2CH), 129.5 (Ar, CH), 129.3 (Ar, 2CH), 128.5 (Ar, 2CH), 128.4 (Ar, CH), 126.9 (Ar, 2CH), 124.3 (=CH), 21.4 (Me); IR ($CHCl_3$): ν = 1712, 1684, 1652, 1612 cm^{-1}; HRMS (ES): calcd for $C_{25}H_{20}O_2$ [*M* + H]$^+$: 353.1536; found: 353.1543.

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Keywords: allenes • enones • heterocycles • regioselectivity • synthetic methods

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[9] CCDC 1413458 contains the supplementary crystallographic data fo compound **5d** in this paper (www.ccdc.cam.ac.uk/data_request/cif).

[10] If this mechanistic picture is operative, cyclization of intermediates **8** coul also occur at another terminus of the allyl cation moiety leading to pyrroles However, we did not observe the formation of pyrroles. Final products, 2-pyrrolines **4**, are stable under the reaction conditions, despite that the undetected pyrroles seem thermodynamically more stable.

[11] According to reference [3c], it is expected to afford methylenecyclopropane intermediates. However, we were not able to detect the formation of these species as byproducts.

[12] Experimental procedures as well as full spectroscopic and analytical data for compounds not included in this Experimental Section are described in the Supporting Information. It contains compound characterization data, experimental procedures, and copies of NMR spectra for all new compounds.

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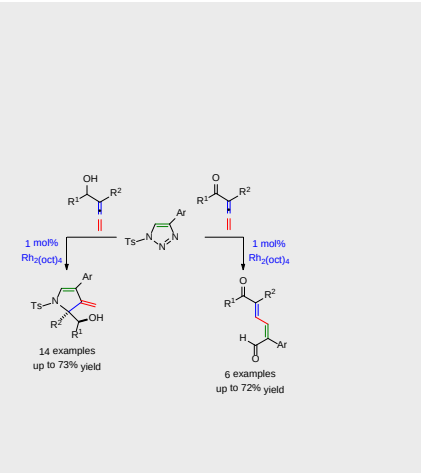
FULL PAPER

The rhodium-catalyzed reaction of 1-benzenesulfonyl-4-aryl-1,2,3-triazoles with functionalized allenes, namely allenols and allenones, has selectively afforded in a divergent way, 2-pyrrolines and 6-oxo-hexa-2,4-dienals.



Synthetic Methods

Benito Alcaide, Pedro Almendros,* Sara Cembellín, Teresa Martínez del Campo, and Guillermo Palop*

■■ – ■■

Allenols versus Allenones: Rhodium-Catalyzed Regiodivergent and Tunable Allene Reactivity with Triazoles