Synthetic Methods

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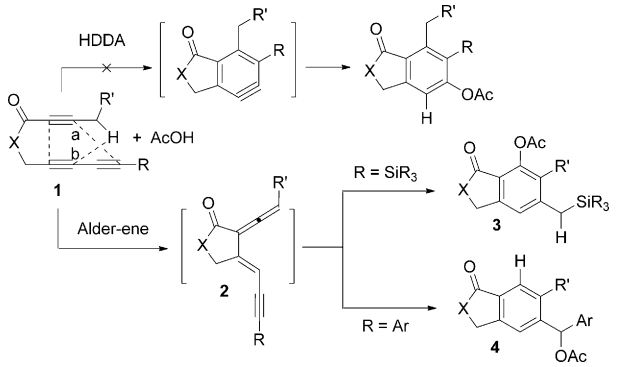
Benzannulation of Triynes to Generate Functionalized Arenes by Spontaneous Incorporation of Nucleophiles**

Rajdip Karmakar, Sang Young Yun, Jiajia Chen, Yuanzhi Xia, and Daesung Lee**

Abstract: *The thermal reaction of ester-tethered 1,3,8-triynes provides novel benzannulation products with concomitant incorporation of a nucleophile. Evidence suggests that this reaction proceeds via an allene-enyne intermediate generated by an Alder-ene reaction in the first step. Depending on the substituent of the alkyne moiety on the allene-enyne intermediate, the subsequent transformation can take one of two different paths, each leading to discrete aromatization products. The benzannulation of a silane-substituted 1,3,8-triynes provides arene products with a nucleophile incorporated onto the newly formed benzene core, whereas an aryl substituent leads to nucleophile trapping at the benzylic carbon atom connected to the aryl substituent. The formation of these two different products results from the involvement of two regioisomeric allene-enyne intermediates.*

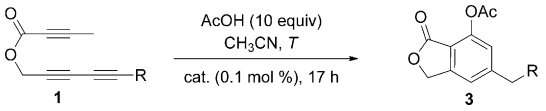


Scheme 1. New benzannulation reactions of ester-tethered triynes.

Benzannulation, that is, the construction of benzene rings from acyclic building blocks, is a versatile approach for the preparation of functionalized arenes, and various synthetic methods are documented in the literature.[1,2] While studying[3] the scope of the benzannulation reaction of ester-tethered 1,3,8-triynes, an unprecedented pathway initiated by an Alder-ene process to form benzannulated products turned out to be preferred over the expected hexadehydro Diels–Alder (HDDA) reaction[2] (Scheme 1). Under typical thermal conditions at 90 °C, the triyne **1** favorably undergoes an Alder ene reaction to form the allene-enyne intermediate **2** as long as there is an available propargylic C–H bond, and then leads to either the benzannulated product **3** or **4** depending on the substituent (R) on the alkyne moiety of **2**. Based on this initially observed reactivity and selectivity feature of the transformation, we further explored the scope of the reaction by employing various ester- and sulfonimide-tethered 1,3,8-triynes. Herein, we describe the outcomes of our investigation on this novel benzannulation reaction focusing on the role of substituents and nucleophiles for the formation of isomeric products.

Our investigation commenced with an optimization of the reaction conditions and the substrate structure in terms of the silyl substituent on the 1,3-diyne moiety (Table 1). It was found that the solvent and temperature of the reaction have a significant impact on the efficiency for the formation of **3a** from **1a**. At 90 °C in CH_3CN, the yield was acceptable (54 %) but a substantial amount of by-product was observed by NMR spectroscopy (entry 1). Lowering the temperature to 60 °C under microwave irradiation for 1 hour afforded only 20 % yield of **3a** (entry 2). To our delight, however, running the

Table 1: Benzannulation of triynes containing various silyl groups in different solvents and temperature.



Entry		R	*T* [°C]	Cat.	Yield [%][a]
1	**1a**	$SiEt_3$	90	none	54
2	**1a**	$SiEt_3$	60	none	20[b,c]
3	**1a**	$SiEt_3$	90	Grubbs II[d]	63
4	**1b**	$SiMe_2tBu$	90	Grubbs II	98[e]
5	**1c**	$SiiPr_3$	90	Grubbs II	68
6	**1d**	$SiPh_3$	90	Grubbs II	52

[a] Yield of isolated product. [b] Incomplete reaction. [c] Under microwave irradiation. [d] Other ruthenium complexes such as $[CpRu(MeCN)_3]PF_6$ and [Cp*RuCl(cod)] mainly provide an unidentified dimeric product. [e] 46 % yield in the absence of Grubbs II. cod = 1,5-cyclooctadiene, Cp = cyclopentadienyl, Cp* = C_5Me_5.

[*] R. Karmakar, Dr. S. Y. Yun, Prof. D. Lee
Department of Chemistry, University of Illinois at Chicago
845 West Taylor Street, Chicago, IL 60607 (USA)
E-mail: dsunglee@uic.edu
J. Chen, Prof. Y. Xia
College of Chemistry and Materials Engineering
Wenzhou University
Wenzhou, Zhejiang Province 325035 (P.R. China)
E-mail: xyz@wzu.edu.cn

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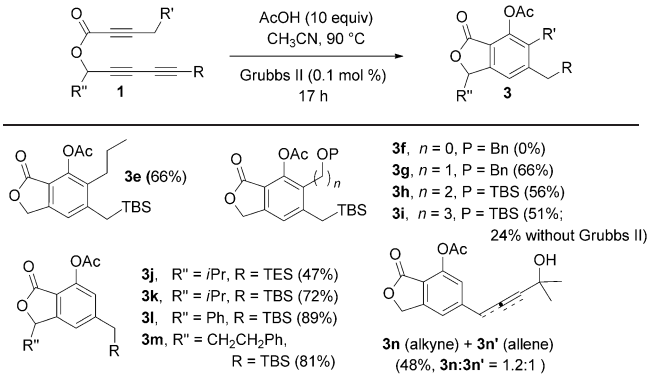
reaction at 90 °C in CH_3CN with a small amount (0.1 mol %) of the Grubbs second-generation complex (Grubbs II) suppressed the formation of the unknown by-product,[4] thus improving the yield of **3a** to 63 % (entry 3). Further improvement was achieved when the triethylsilyl (TES) group of **1a** was replaced with *tert*-butyldimethylsilyl (TBS) group (**1b**) under identical reaction conditions, thus leading to **3b** in 98 % (entry 4). In contrast, the triisopropylsilyl (TIPS) group in **1c** or triphenylsilyl (TPS) in **1d** had a marginal improvement, thus providing the corresponding products **3c** and **3d**[5] in 68 and 52 % yield, respectively (entries 5 and 6).

Having defined the optimal silyl functionality in the substrate and assorted reaction conditions, we explored the reaction of substrates containing more substituents in the ester-tethered triyne platform (Table 2). The reaction of **1e**,

Table 2: Benzannulation of ester-tethered 1,3,8-triynes.[a]

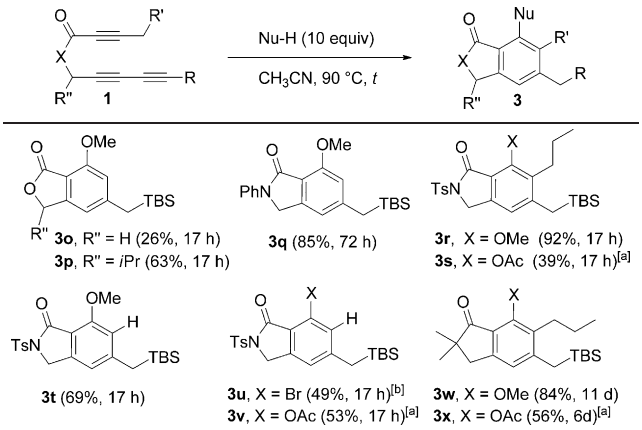


[a] Numbers within parentheses represent yield of the isolated products.

with an extra propyl substituent (compared to **1a**), afforded the expected product **3e** in 66 % yield. Although **1f**, with a benzyloxy substituent at the propargylic carbon atom, did not yield the product **3f**, its homologue **1g** and silyloxy-substituted substrates **1h** and **1i** produced the expected products **3g–i** in 66, 56, and 51 % yield, respectively. The slightly lower yields from **1h** and **1i** are most likely due to its instability under the reaction conditions. Introducing a substituent at the propargylic site of the 1,3-diynyl moiety did not change the reactivity of substrates **1j–m**, thus the products **3k–m**[5] were obtained in yields in the range of 72–89 %, but only 47 % for **3j** because of its labile TES group. Replacing the silyl group with another alkyne in **1n** led to the formation of a mixture of **3n** and **3n′** in 48 % yield.

To broaden the scope of the reaction, we employed an assortment of substrates of different tethers and trapping agents (Table 3). Upon heating **1b** at 90 °C in MeOH, the benzannulation product **3o** was obtained in 26 % yield and accompanied by the methanolysis product 1,3-diynyl propargylic alcohol in 50 % yield. The sterically hindered ester **1k** (R″ = *i*Pr), however, afforded **3p** in 63 % yield without methanolysis.[6] Replacing the ester linkage with an amide improved the yield, although a longer reaction time was required. For example, the triyne **1q** produced **3q** in 85 % yield after heating for 72 hours. Replacing the phenyl group in **1q** with a more-electron-withdrawing sulfonimide moiety in

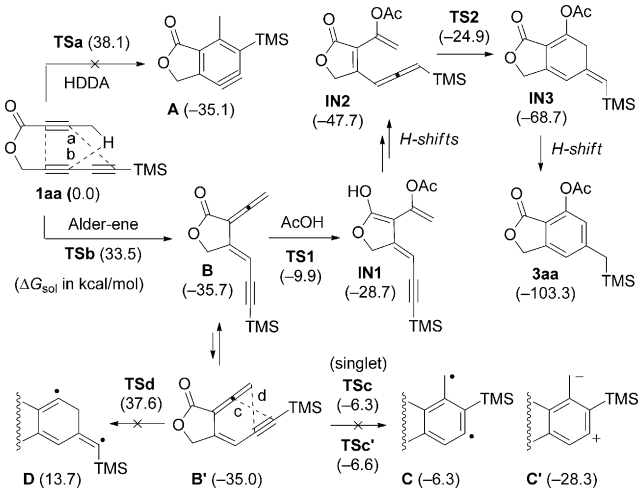
Table 3: Benzannulation of triynes with different tethers in the presence of various nucleophiles.



Numbers within parentheses represent yields of the isolated products. [a] Grubbs II (0.1 mol %) was used in these reactions. [b] With a bromide source described in Ref. [2c]. Ts = 4-toluenesulfonyl.

1r significantly improved the reaction profile, thus providing **3r** in 92 % yield within 17 hours. However, only low yield of **3s** (39 %) was observed when AcOH was used as a trapping agent. To our surprise, the substrate **1t** (R′ = *t*Bu) yielded **3t** which was devoid of the *tert*-butyl group. The reaction of **1u** with a bromide nucleophile afforded the aryl bromide **3u** in 49 % yield, and the same substrate in the presence of AcOH as a nucleophile produced aryl acetate **3v** in 53 % yield. Substrates having a ketone linkage can also undergo a benzannulation reaction only when a *gem*-dialkyl moiety is present. Thus, the benzannulation products **3w** and **3x** were obtained in the presence of MeOH and AcOH respectively, albeit after prolonged heating.

To gain insight into the mechanism of this benzannulation, we carried out DFT calculations[7] (M06-2X/6-31 + G* level[8]) with the triyne **1aa** as a model system (Scheme 2). Calculations clearly indicate that the ene reaction leading to the alkynyl enallene **B**[9] is kinetically more favorable by 4.6 kcal mol^{-1} than the HDDA reaction leading to the aryne **A**. Under the reaction conditions, **B** isomerizes to **B′**, from which cyclization occurs to form **C** and **D**. The Saito–Myers cyclization[1e,g,h,r] of **B′** to form **C** via **TSc** (−6.3 kcal mol^{-1})[10] or its ionic version to form **C′** via the slightly lower-energy **TSc′** (−6.6) is energetically reasonable but it does lead to incorrect connectivity. However, the formation of the diradical **D**, bearing the correct connectivity of the observed product via **TSd** (37.6 kcal mol^{-1}), does not seem feasible from either a kinetic or thermodynamic aspect.[7,11] This energetic consideration suggests an alternative mechanism involving the Michael addition of AcOH to the allenoate moiety of **B**,[12] where the barrier (**TS1** = −9.9 kcal mol^{-1}) leading to **IN1**, albeit slightly endergonic, is 3.3 kcal mol^{-1} lower than even that of the Saito–Myers cyclization (**B′**→ **C**).[13] From **IN1**, all the remaining steps, involving proton-shift-mediated relocation of π bonds to form **IN2**, its 6π electrocyclization[14] to form **IN3**, and aromatization by a formal [1,3]-H shift leading to **3aa**, seem to be quite reasonable energetically.

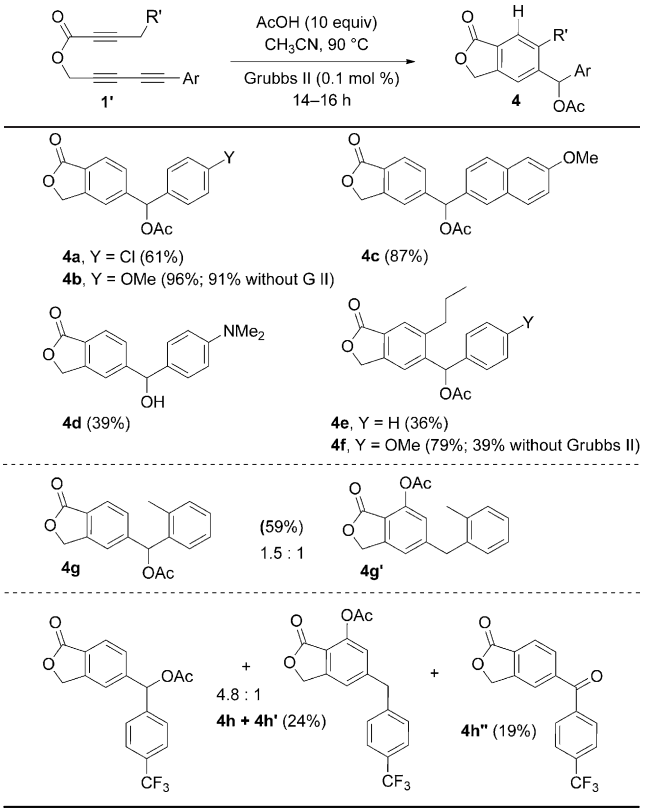


Scheme 2. DFT-based mechanistic rationale.[7]

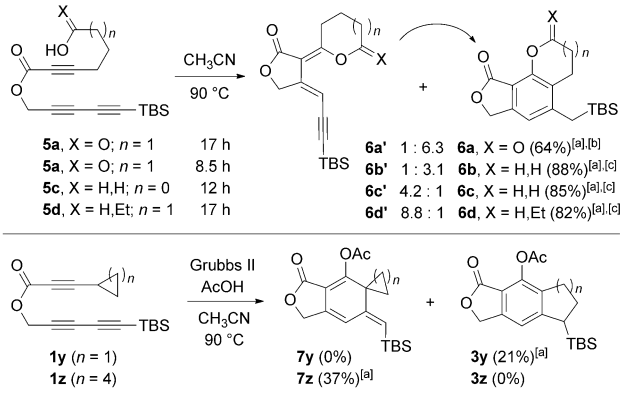
With this mechanistic rationale in hand, we tried to diversify the substrate structure, thus surmising that replacing the silyl group on the 1,3-diyne moiety with other functional groups should not profoundly alter the reaction profile. To our surprise, however, the benzannulation of the triynes **1′**, containing an aryl group, provided the compound **4** which contains an incorporated acetate at the bis-benzylic carbon atom rather than on the newly formed benzene ring (Table 4).[15] The reaction was found to be sensitive to the electronic nature of the aryl group, where an electron-donating group afforded higher yield of the products. For example, **4a**, with a 4-chloro substituent, was isolated in 61% yield while **4b**, containing a 4-methoxy group, was obtained in 96% yield. Also, a substrate containing a methoxy-substituted naphthyl group gave **4c** in 87% yield. In contrast, the substrate with a 4-dimethylamino group afforded the alcohol **4d** in 39% yield. Probably, the amino group, upon protonation by acetic acid deactivates the substrate yet promotes the hydrolysis of the acetate during purification by silica gel column chromatography. An extra alkyl substituent (R′) in **1′** is detrimental to the benzannulation, thus **4e** and **4f** were isolated in lower yield. The beneficial role of the Grubbs catalyst in these reactions was clearly demonstrated in the formation of **4f**. Introducing an *ortho*-substituent on the aryl moiety produced a mixture of two isomers, **4g** and **4g′**, in a combined yield of 59%. A substrate with an electron-withdrawing substituent on the aryl ring produced a mixture of isomers, **4h** and **4h′**, in low yield along with an unexpected diarylketone product **4h″** in 19% yield.[5]

Next, we explored double annulation reactions by employing intramolecular trapping and ring expansion approaches (Scheme 3). Upon subjecting **5a–d** to the standard reaction conditions (CH_3CN at 90°C), the compounds **6a′–d′** were isolated along with double annulated products **6a–d** in varying ratios. Although the carboxylic acid adduct **6a′** is unstable,[16] the corresponding alcohol adduct **6b′** is relatively stable, and rearranges into **6b** quantitatively over a 3 day period at room temperature, and **6c′** rearranges into **6c** only at high temperature (120°C, 9 days). Monitoring of the reaction of **5d** by ^{1}H NMR spectroscopy indicates that its

Table 4: Benzannulation of triynes with an aryl substituent.[a]



[a] Numbers within parentheses represent yields of isolated products.



Scheme 3. Double annulation reactions: [a] Yields are those of isolated products. [b] Yield of **6a** + **6a′**. [c] Yield after complete conversion.

conversion into **6d′** is fast at 90°C but the conversion of **6d′** into **6d** is slow (4 days) at this temperature. The isolation of **6a′–d′** and their conversion into **6a–d** suggest that they are a true intermediate for the benzannulation reaction.[17]

The substrates **1y** and **1z** were employed to test the feasibility of a double annulation (Scheme 3). As expected the initially formed mono-benzannulated vinyl cyclopropane intermediate **7y** undergoes a ring expansion through a 1,3-alkyl shift to generate the indene derivative **3y**.[18] In contrast, the reaction of **1z** afforded only **7z**, which is stable and did not rearrange to the aromatized product **3z** under the reaction

conditions, even after a prolonged reaction time. These results also provide strong support for the reaction mechanism involving the intermediate **IN3** in Scheme 2.

In summary, we have discovered the benzannulation of 1,3,8-triynes under thermal conditions to generate highly functionalized arenes. This reaction proceeds through an initial Alder-ene reaction to form an allenoate intermediate with subsequent Michael addition of a nucleophile. Subsequent π-bond migrations to form a conjugated diene-allene system then sets the stage for an electrocyclization and a formal 1,3-H shift, thus providing nucleophile-incorporated arene products. Depending on the substituent of the alkyne moiety on the allenoate intermediate, the subsequent transformation takes one of different pathways. The allenoate derived from either silane- or alkyne-substituted 1,3,8-triynes favors the nucleophile addition at an earlier stage, as supported by DFT calculation, thus leading to benzannulation products with an incorporated nucleophile on the newly formed benzene core. In contrast, the reaction of the aryl-substituted 1,3,8-triynes provided benzannulation products with a trapped nucleophile at the benzylic carbon atom connected to the aryl substituent. This divergence seems to be the consequence of the formation of a regioisomeric allene-enyne intermediate. Investigation on the mechanism of the latter pathway is underway.

Keywords: annulation · arenes · rearrangement · regioselectivity · ruthenium

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[4] The Grubbs second-generation complex is used as a catalyst when AcOH is the trapping agent, wherein we believe the ruthenium complexes catalyzes the isomerization of **B** to **B′** in Scheme 2. Although the role of these complexes is yet to be further elucidated, it generally reduces the formation of unknown by-products. See the Supporting Information for details.

[5] The structures of **3d** (CCDC 1040777), **3l** (CCDC 1040778), and **4h″** (CCDC 1040779) were confirmed by X-ray diffraction analysis. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[6] A methanol adduct similar to those described in Scheme 3 was isolated in 39% yield. See the Supporting Information for details.

[7] All reported energy values are relative free energies including solvation corrections. See the Supporting Information for details.

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[10] A higher barrier (**TSc** = 15.7 kcal mol^{-1}) is calculated for more stable triplet biradical (−33.4 kcal mol^{-1}).

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[13] The Michael addition of HOAc to **B′** is 1.4 kcal mol^{-1} higher in energy than **TS1**.

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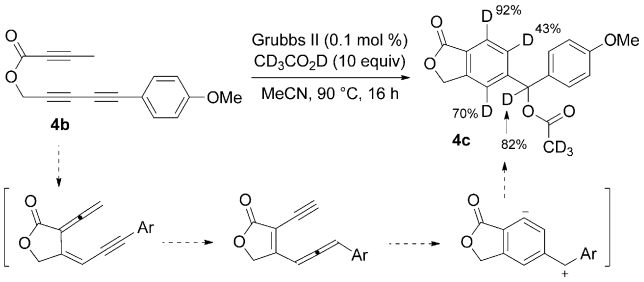
[15] The mechanism for the formation these products is yet to be elucidated but at least it is not consistent with the pathway involving **B**→**B′**→**D**, based on the unusually high calculated activation barrier (72.6 kcal mol^{-1}) and the deuterium incorporation pattern in **4c**. Relying on several lines of evidence, we

tentatively propose that with an aryl substituent, **B′** favorably rearranges to a regioisomeric allene-enyne (a consequence of a formal [1,7]-H shift), which then undergoes an ionic Saito–Myers cyclization to generate a zwitterionic intermediate, the trapping of which provides the observed product.



[16] The compound **6a′** does not have a long enough lifetime for ^{13}C NMR spectroscopy, and it readily converts into **6a**.

[17] Similarly, the methanol adduct mentioned in Ref. [6] was converted into the corresponding benzannulated product under three different conditions. See the Supporting Information for details.

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Communications

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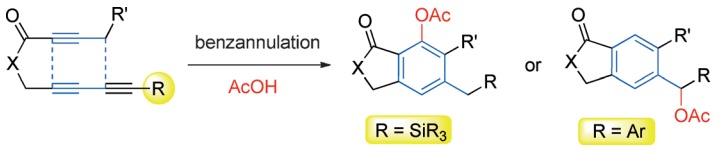
R. Karmakar, S. Y. Yun, J. Chen, Y. Xia,*
D. Lee* ——————— ■■■■–■■■■

Benzannulation of Triynes to Generate Functionalized Arenes by Spontaneous Incorporation of Nucleophiles



Small but profound: In the benzannulation reaction of 1,3,8-triynes, a small structural difference has a profound impact on the structure of the products. When R is a silyl group, a nucleophile is incorporated into the newly formed benzene core, whereas when R is an aryl group, nucleophile trapping occurs at the benzylic carbon atom connected to the aryl group.